ELEMENTARY
PRINCIPLES
OF CHEMISTRY
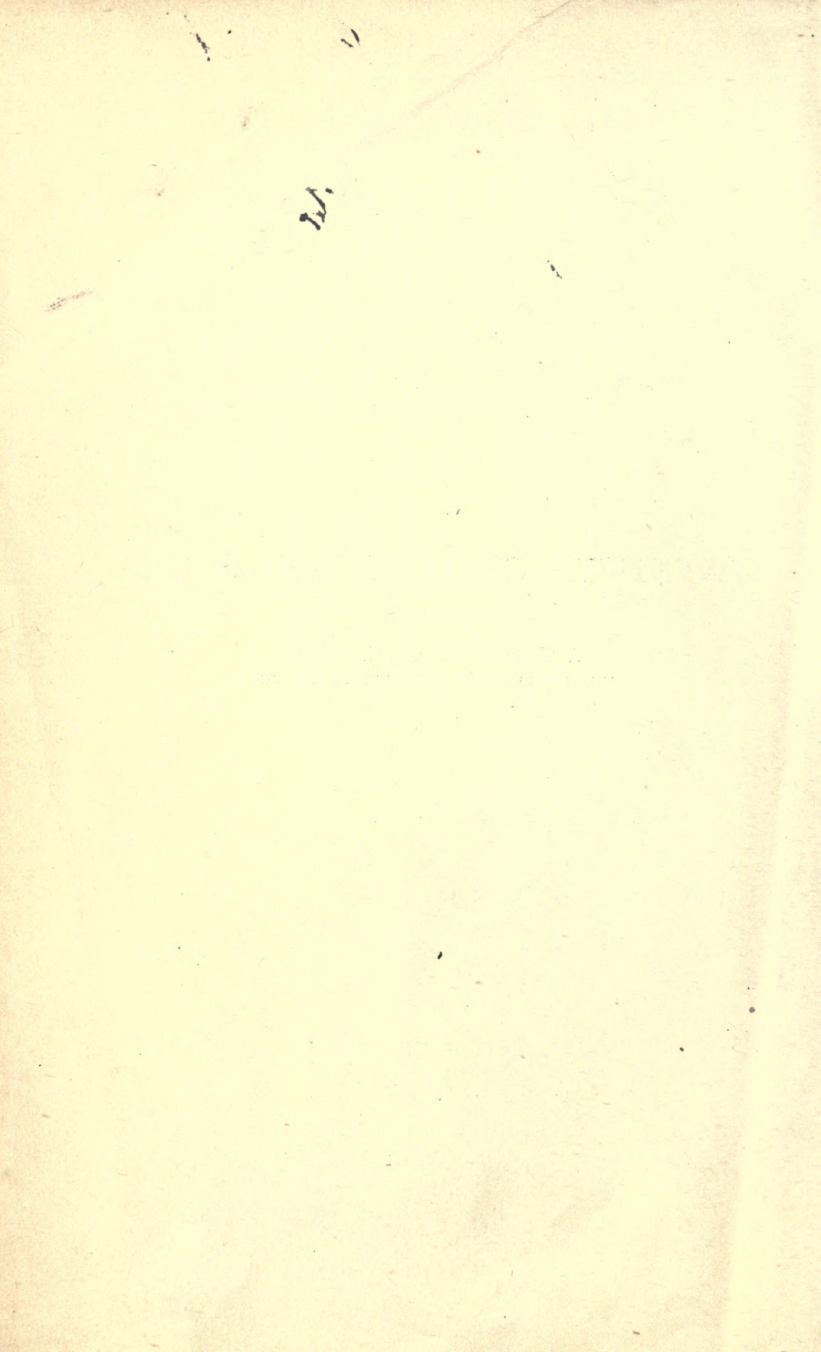
TWENTIETH CENTURY TEXT-BOOKS

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THE
ELEMENTARY PRINCIPLES
OF CHEMISTRY

BY

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"Not blind
To worlds unthought of till the searching mind
Of Science laid them open to mankind"
WORDSWORTH

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PREFACE

THIS book on elementary chemistry is based on the plan which, without essential modification, the writer has been following for thirteen years with his classes beginning the subject. Its inception was under the stimulating suggestion of the late Professor Josiah P. Cooke, of Harvard University, an early advocate of what has been called the quantitative method in teaching the subject even in elementary courses. The temerity of the writer in thus offering to his fellow-students and teachers the outcome of his personal experience is due to the hope, perhaps egotistic, that he may contribute, in howsoever small a measure, to making practicable and serviceable that which, he enthusiastically believes, is both scientifically and pedagogically an improvement on the older and still largely prevailing method.

In the preparation of the book two things have been assumed : first, that sufficient laboratory facilities are provided ; and, second, that the teacher has information in the subject beyond that which the book itself supplies. The laboratory work by the student is made a large and essential part of the exposition, and it is generally assumed that he has performed the experiment illustrative of a topic before he gives attention to the fuller presentation of the same in the text. 84369

The writer fully appreciates the increased demand made by such a course on the teacher's time and strength, and he has therefore prepared to accompany this book a teacher's aid, in which he has put whatever he has been able of suggestions which may be helpful and labor-saving to the teacher, but which do not suitably find place in a book designed for the use of students.

A. V. E. Y.

Evanston, Ill., *June, 1900.*

FOREWORD TO THE STUDENT

You are about to enter upon the study of a branch of natural science, perhaps the first to which experience has brought you. If I am to have the privilege, shared with your teacher, of being your guide in this, I beg the additional privilege of addressing a word to you, at the outset of your study, in a purely personal manner and free of the formality of authorship. As a lover of nature, whether in the aspect revealed by science, or in that which lies open to him who has eyes to see and soul to feel, and as one to whom science study has brought much genuine enjoyment, I would that to you also this study might be not a task only, even though interesting and profitable, but a source of real pleasure.

A large portion of your time will be given to experiments. They may seem tedious at times, and may test your patience; but they are designed to teach, not to amuse, and, in order to teach, they must be performed studiously and thoughtfully. It may be hoped that you will find a pleasure added to mental activity in the accompanying use of the hands.

Again, your experiments are generally to be thought of as giving you not proof of laws, but illustration, as aid to clear ideas. In my own classes, I like that the student

should, so far as practicable, get the first notion of a topic through his own observation, instead of being told in previous explanation what he is to see. In this way, I believe, there may come to him just a taste of the keen pleasure of discovery that comes to the investigator and pioneer.

I would reckon one opportunity of profit from a course in physical science as lost to that student who fails to acquire some increased measure of respect for the teachings of experience, which should serve him to good purpose, if rightly applied, in the daily conduct of life.

Moreover, he should learn respect for material things, finding in them not alone facts, useful of application in practical life, and gratifying to the inborn curiosity of the human mind to know, but likewise things worthy of oft-repeated contemplation, and gratifying to the intellect to admire. The lover of nature is not content with one view of a beautiful landscape; nor is the lover of art content with one look at the handiwork of a great painter or sculptor, but he returns with fresh joy to contemplate the beauty which it embodies. Yet this is the work of the human hand and intellect. Likewise the student of natural science, I am sure, may, if he will, add much to the pleasure of his work and to its ennobling influence by finding in the material things revealed by his science the handiwork and embodied thought of the mightiest of creators, worthy of repeated contemplation and productive of the noblest pleasure.

> " God is the Perfect Poet,
>> Who in creation acts his own conceptions."
>>> ROBERT BROWNING, in Paracelsus.

A. V. E. Y.

SCHEME OF TOPICS

[The numbers following the topics refer to marginal numbers in the text, which are the same for the same topics in both Part I and Part II.]

CHAPTER I. Nos. 1–33

INTRODUCTORY

In Physical Phenomena two things distinguished :
>*Matter* and *Energy*.
>Different kinds of Matter = *Substances*.
>Transformation of Substances.

Definition and Identification of Substances by Physical and Chemical Properties

A. Physical Properties (with special reference to Identification) :
1. Taste.
2. Odor.
3. Relative Hardness.
4. Form (crystalline).
5. Mass (measured by weight).
6. Volume.
7. Specific Gravity, No. 7.
    (Comparative weight.)
8. Behavior toward Light :
    As to Color, Luster, Transparency, Opacity.
9. Behavior toward Electricity.
10. Behavior toward Magnetism.
11. Behavior toward Heat
    a. Solids.
        Fusion, solidification, 10.
    b. Liquids.
        Boiling, 11.
        Distillation, 12.
        Sublimation, 12.
    c. Gases.
        Burning or combustion.
        Chemical change.

B. Chemical Properties, 13.
    Transformation of Substances.
    Behavior toward Other Substances.
C. Physico-Chemical Properties.
    1. Allotropism, 13.
    2. Solution, 21.

            Study of Chemical Change, 15–18.

          Additional Physical Properties
Crystallization, 21/₄.
Amorphism, Polymorphism, Isomorphism, 21/₆.
    Water of Crystallization, 21/₇.
Efflorescence, 21/₈.
Deliquescence, 21/₈.
    (Hygroscopic.)
Heat of Solution, 22.
Melting Point, 23.
    Freezing Point.
    Surfusion.
Boiling Point, 24.
    Conditions affecting.

          Chemistry is both :
A. Static.
    Description, Identification, Classification of Definite Chemical
        Substances.
    Qualitative Analysis, 26.
    Quantitative Analysis, 26.
B. Dynamic, 26.
    Factors
    Products
    Laws   Chemical Change, or
    Agency—i. e.,   of Reaction, or
      Chemism or Chemical Affinity   Interaction.
    Energetics
          All Substances classified into :
a. Elements, 27, and
b. Compounds (Mechanical Mixtures, 28).
    Compounds classified (in part), 30 :
        Acids, Bases, Salts.
          Chemical Changes classified (in part), 31 :
a. Analytic (Decomposition).
b. Synthetic (Combination).
c. Metathetic or Mixed (Exchange).
    Substitution.

THE ELEMENTARY PRINCIPLES
OF CHEMISTRY

PART I

CHAPTER I

INTRODUCTION

Matter, energy, substances.—In physical phenomena the 1*
student of nature has learned to distinguish two things,
Matter and *Energy*. Matter is all that which occupies
space, has weight, and is acted upon by various agents;
for example, earth, water, air, iron, wood, and salt. Energy
is that which brings about change in things; change in
position—that is, motion—as when a body falls to the
earth; or change in nature, as when iron rusts, or wood
burns, or water freezes. Energy is therefore the general
name, not for any particular agent, but for all agents that
bring about the specified changes. Thus, gravitation, heat,
electricity, magnetism, and light are only different forms
or conditions of energy. Likewise, the very many things
familiarly recognized, such as water, air, coal, copper, silver,
gold, and others not so familiar, are simply different kinds
of matter; to designate these is used the term, *substances*.

Substances are not permanent.—Now, it is readily recog- 2
nized as a fact of common observation, that substances, in
many instances at least, are not permanent, but are subject

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* The marginal numbers are the same for the same topics in both
Part I and Part II.

to change; and furthermore, that the changes often result in the disappearance of the original substances. Thus water may lose its liquid form and become solid, in which condition we call it ice; or it may become gaseous, in which condition we call it steam or vapor. Wood rots and iron rusts, and in so doing both lose many of the properties which make them useful. Wood and coal burn, and thus are converted into something which is neither wood nor coal. A lump of sugar, or of salt, when dropped into water, completely disappears so far as we can see. And many similar observations might be cited. But, evidently, we can not make even the simple observation that iron ceases to be iron when it rusts, or that wood ceases to be wood when it burns, or, in general, that any substance, A, ceases to be A, or becomes some other substance, B, unless we have some means of identifying the substances, A and B, and distinguishing between them; and these constitute, in part at least, the subject-matter of Chemistry. For present purposes, then, we may define Chemistry as that branch of physical science which deals primarily with the properties and transformations of substances. Physics, on the other hand, deals primarily with the several kinds of energy and their transformations. The two sciences are therefore closely related, and many phenomena may be considered as properly in one as in the other; and some must, indeed, be considered in both.

3   **Identification of substances.**—We proceed, therefore, to study somewhat in detail the identification of substances. Broadly speaking, a substance can be identified only by its totality of properties, but in practice it is possible to use selected properties, since we have learned by experience that these are accompanied by the others which make up the total. Of the properties of a substance, we designate as *physical* those which involve no change in the identity of the substance; as *chemical*, those which do involve such change. But here, as often when we attempt to classify

or define the things of nature, we find those which can not be placed satisfactorily in one or the other class, since they partake of the character of both ; and so we shall find it convenient to recognize properties of a third class, and to designate them as the *physico-chemical*.

1. Physical Properties

Among the physical properties useful for identification 4 may be cited : taste, odor, relative hardness, form (crystalline), specific gravity (i. e., the relation between weight and volume) ; also behavior toward (1) light, as to color, luster, opacity, etc. ; (2) toward electricity ; (3) toward magnetism ; (4) toward heat.

The chemical properties may be described, with but few 5 exceptions, as the behavior toward other substances ; while the phenomena of solution and of allotropism may serve as illustrations of physico-chemical properties.

Before presenting formal statements and definitions concerning these items, it is best that they be studied by practical illustrations ; and so sulphur is taken up first, as an object-lesson in description and identification of substances (see Chapter I, Part II). Following the observations and illustrative experiments made by the student in the laboratory, the matter now to be presented may be considered as a review and summary of the corresponding topics, with some added information, impracticable of illustration.

Taste.—Taste is of limited applicability for purposes of 6 identification, and in the chemical laboratory should be used with only the utmost caution, as many substances are extremely poisonous.

Odor.—Odor is more often serviceable, but likewise must be used with caution.

Form.—By form in this connection is meant only crystalline form—that is, definable, geometric form, which, as will be seen later, is often characteristic.

2

7   Specific gravity.—The specific gravity of a substance is the ratio of the weight of some sample of it divided by the weight of an equal volume of some standard substance. Water is taken as the standard for solids and liquids, or, more strictly speaking, water at its maximum density (temperature 4° C.). For gases, both hydrogen and air are used ; the former is preferred in this study, and may be understood as the standard for gases unless it is otherwise specified. Inasmuch as the specific gravity of air referred to hydrogen is 14.40, it is easy to pass from one scale to the other by the use of this factor.

8   Your experiment with sulphur has given illustration of a method for determining the specific gravity of solids which are not soluble in water. If the solid dissolves in water, some other liquid must be used in which the substance is insoluble, and of which the specific gravity is known. Another method is based on the principle that a body when suspended and immersed in a liquid weighs less than when weighed in air simply, and less by a quantity equal to the weight of the liquid displaced.

Since liquids and gases may completely fill their containing vessel, their specific gravity may be determined by weighing successively the vessel when empty, when filled with the standard, and when filled with the substance in question.

9   Electrification.—The electrification of sulphur by friction, so that it attracts particles of matter, is a minor item. Of the same order also, is the familiar observation that iron is attracted by the magnet.

The facts as to color, luster, opacity, or transparency usually appear simply on inspection.

10   Behavior toward heat.—The behavior toward heat is of prime importance. Three conditions of matter are recognized—the solid, the liquid, and the gaseous. These are dependent on the temperature, or on the temperature and the pressure combined.

Fusion or *melting* is changing a solid into a liquid by the agency of heat. *Freezing, solidification,* or *congelation* is changing into the solid condition from the liquid, sometimes from the gaseous, by the withdrawal of heat. The behavior of sulphur, which you have noted, is peculiar in that the continued application of heat after fusion causes the liquid first to become semi-solid and then to regain its fluidity. The temperature at which fusion and solidification take place is definite and constant for a given substance, and hence offers a valuable feature for identification. Its determination will be considered later.

Boiling or *ebullition* is the formation in a liquid of bubbles of its own vapor. Evaporation—that is, the conversion of a liquid into vapor at its surface only—takes place at indefinite temperatures, even much below that of boiling. But bubbles of vapor form only in definite conditions, and therefore the temperature at which boiling takes place is also a valued feature, which later will be studied in detail. **11**

Distillation (for experimental illustration see not only Exps. 11 and 12, but also $20/_1$ and $24/_5$, and Appendix, 18) is the conversion of a solid or of a liquid into vapor by heating, and this vapor in turn into a solid or liquid by cooling. It is serviceable in separating volatile from non-volatile substances, or substances differing in degree of volatility, and is therefore often a valuable means of purification. That which is separated by distillation and condensed is called the *distillate*. Some substances may be converted from solid to vapor and back to solid without passing through the liquid condition. This operation is called *sublimation*, and the condensed portion is called the *sublimate*. **12**

In nature the formation of rain may be considered as distillation on an enormous scale, since water passes from the surface of the sea and other bodies of water into the atmosphere as a vapor, is subsequently condensed into liquid form, and falls to the earth again as drops of rain. Or, the water vapor of the atmosphere may condense

directly to the solid snowflake or to the frost upon the window pane, and these we may think of as natural sublimates.

Distillation and sublimation are used also in many industrial operations—for example, in the manufacture of alcohol, the refining of petroleum, of sulphur, and of iodine.

2. Chemical Properties

13   **Essential feature.**—Returning to the observations with sulphur: you have seen that, if the heating is continued beyond the boiling point, the sulphur finally takes fire, burning with a pale bluish flame; that in consequence of this change, called *combustion*, the sulphur disappears; that a substance appears which is gaseous at the ordinary temperature, has a peculiar, stifling odor, changes blue litmus paper to red, and is thus a substance distinctly different from the sulphur itself. This change is a chemical one, its essential feature being *the production of a substance other than the original—it is a change of identity ;* whereas the other changes already noted, electrification, fusion, solidification, boiling, sublimation, and distillation, all physical, have left the substance still sulphur. The peculiar product obtained by turning the liquid sulphur at about its boiling point into cold water certainly differs in some of its properties from the original substance. On inspection you hardly recognize it as sulphur, yet on standing it passes back into the brittle condition without a change in weight, and on burning it yields the same gaseous product that the brittle sulphur does. Such a change, considerable yet not sufficient to constitute a change in identity, is called *allotropic ;* and the plastic or amorphous substance and the brittle or crystalline are said to be allotropic forms of sulphur. Further illustration of chemical change you have seen in the production of iron sulphide from iron and sulphur, zinc sulphide from zinc and sulphur, hydrogen sulphide from hydrochloric acid and iron and zinc sulphides.

Secondary features.—You may also note as secondary 14 differences between physical and chemical changes, that the former may involve but a single substance, whereas chemical changes must involve at least two, and generally involve more than two. There are a few, but only a few, changes which fall under the general form : substance A becomes substance B, or, more briefly expressed, $A = B$. Therefore the chemical properties of a substance may be generally described as its behavior toward other substances. Again, the physical changes are often reversible by reversing the conditions ; thus sulphur changes from solid to liquid and then to vapor by rise of temperature, and then a fall of temperature reverses the changes. On the other hand, if the temperature be raised until the sulphur burns —that is, until chemical action takes place and the new substance, sulphur dioxide, is formed—this change is not reversible ; that is, the sulphur can not be recovered by cooling the gas.

3. Additional Illustrations of Chemical Change

The additional illustrations of chemical change have brought to your attention the four types, which may be given general expression in the following concise equation forms, and which for the present have been sufficiently dwelt upon in connection with the illustrative experiments :

(1) $A + B = AB$ (composition). 15
(2) $AB = A + B$ (decomposition). 16
(3) $A + BC = B + AC$ (substitution). 17
(4) $AB + CD = AC + BD$ (double exchange). 18

4. Additional Illustrations of Physical Properties

Solution.—We proceed now further to consider some of 21 the physical properties. *Solution* is the conversion of a solid or of a gas into a liquid by the action of a liquid,

The term is also applied to the mixing of one liquid with another. The substance dissolved is called the *solute*, the liquid which effects the solution the *solvent*, and, unfortunately for clearness, the mixture of these two—that is, the result obtained by dissolving—is called the *solution*. The phenomenon of solution has practically a limitation, qualitative in character—that is to say, some substances dissolve in some solvents and not in others, while some are practically insoluble in all solvents. Thus sugar, common salt, alum, and copper sulphate dissolve in water, but not in carbon disulphide ; while sulphur dissolves in the latter (see Exp. 12/2), but not in water. And yet those substances commonly reckoned as the most insoluble do, in many instances, dissolve in minute quantity. Thus, for instance, sand, limestone, and glass would in ordinary experience be thought insoluble in water, yet they do appreciably dissolve.

21/1   Solution plays an important part, often on a vast scale, in the processes of nature, and in these, water is the great solvent. Water passing through the atmosphere and over or through the earth's crust dissolves many substances in quantities—small perhaps in proportion to the quantity of the solvent, yet large in the aggregate, since the quantity of water is enormous. These ultimately, at least in large part, reach the sea, which thus becomes a vast reservoir, not only of water, but also of soluble matter from the solid portion of the earth's crust. This is the most stupendous instance of the phenomenon of solution within our observation. In the vital processes of the plant and of the animal, solution is of great importance, serving to bring the constituents of the food into condition suitable for distribution and assimilation in the different parts of the organism.

21/2   Solution is an operation of prime importance also in the industrial arts as well as in the laboratory. It is used not only to separate soluble from insoluble substances and substances of different degrees of solubility, and consequently as a means of purification, but also to bring about a condition suitable for some other operation or change. The refining of sugar is one of the innumerable instances.

21/3   The property of solubility or insolubility, or the degree of solubility, is also of great practical value in the identifi-

cation of substances. The quantity of a given substance which a definite quantity, say one hundred grams, of a given solvent can dissolve is limited, and is dependent on temperature, and, in the case of gases, on pressure also; but for a definite temperature (and pressure) the quantity is definite. The solubility of solids generally increases with increase of temperature, but in some instances it decreases. The solubility of gases diminishes with increase of temperature, and it increases with increase of pressure. A solvent, when it has dissolved the maximum of a given substance, is said to be *saturated*. Unsaturated solutions of solid or non-volatile substances may be concentrated by evaporating the solvent (see Exp. 21/4), and the solute may be recovered, often unchanged, by making the evaporation complete (see Exps. 17/1 b and 18/A).

Crystallization.—If saturated or nearly saturated solu- 21/4 tions remain undisturbed, so that slow cooling and evaporation may take place, the solid in many instances separates in definite geometric forms, as you saw in your own experiments with alum and copper sulphate. This is *crystallization*. It may accompany solidification, not only from the state of solution, but also of fusion (seen in the sulphur experiments, Nos. 11 and 12, and 12/1), and even from the gaseous condition (seen in the experiment with iodine, No. 20/1, the sublimate of which is beautifully crystalline). In the crystallization of mixtures each individual substance crystallizes by itself, in its own peculiar form, and therefore crystallization is a most important means of separation and purification. Furthermore, the peculiarities of form—that is, the shape and disposition of the faces, the dimension of the angles, etc.—are definite and constant characteristics of the substance, and therefore of great value in identification.

.Crystallization on the large scale finds abundant illustration in 21/5 nature, since many constituents of the earth's crust exist in crystalline condition, either in large masses of crystalline structure, like granite,

marble, etc., or as distinct individual crystals like the diamond, ruby, emerald, and many other valued gems. Many manufactured products also appear in crystalline condition, of which sugar and salt may be cited as examples.

21/6   Substances when they do not show this definite geometric or crystalline form are said to be in the *amorphous* condition. Some substances are capable of crystallizing in two or more distinctly different forms. They are said to be *polymorphous*, or, if they exhibit only two forms, *dimorphous*. This property you have seen in the two crystalline forms of sulphur (see Exps. 12/$_1$, and 12/$_2$). On the other hand, some instances are found of different substances exhibiting the same crystalline form, and such substances are called *isomorphous;* examples are calcium, magnesium, iron, and zinc carbonates.

21/7   Many substances, not all, in crystallizing from water solution, contain water as a constituent, although no evidence of this is seen by simple inspection of the crystal. This is termed *water of crystallization.* It can generally be driven off by heating, and the crystalline structure is thus destroyed, as you have seen with copper sulphate. In some instances the crystal first melts in its water of crystallization, as in the case of alum. Substances from which the water has thus been taken and substances which contain no water are said to be *dehydrated* or *anhydrous.* Again,

21/8   some substances lose their water of crystallization at the ordinary temperature; such are called *efflorescent;* examples, sodium carbonate and sodium phosphate. On the other hand, some substances absorb water from the atmosphere and tend to liquefy in consequence; these are described as *deliquescent;* examples, zinc chloride (see Exp. 17/$_1$ b), calcium chloride, and sodium hydroxide. The term *hygroscopic* also is applied to substances which thus absorb water, but this does not imply liquefaction. Thus, common quicklime—that is, calcium oxide—takes water abundantly, but retains the solid form.

Heat of solution.—Solution, when solute and solvent 22
are of the same temperature before mixing, is usually, not
always, accompanied by reduction of temperature. Thus,
common salt dissolving in water lowers the temperature,
while sodium hydroxide and hydrochloric acid raise it.

Melting point.—The *melting point* of a substance is the 23
temperature at which it melts, and the *freezing point* is the
temperature at which it solidifies; and, being definite and
constant characteristics of a specified substance, they are,
as already suggested, useful in description. One would ex-
pect the two temperatures to be really identical, yet obser-
vation shows that the liquid form is sometimes retained
below the melting point. This phenomenon, called *sur-
fusion*, may cause irregularity in the observation of the
freezing point. Your experiment gives illustration of one
method applicable in such observations. With a larger
quantity of the substance, the bulb of the thermometer may
be thrust into the liquid, and the latter be stirred during
the solidification.

The presence of substances in solution tends to lower the 23/1
freezing point of the solution as compared with that of the
pure solvent. This phenomenon will be studied quantita-
tively in Chapter V.

Boiling point, and circumstances affecting it.—The *boiling* 24
point of a substance, defined in the strictest sense for pur-
pose of description, is the maximum temperature which its
vapor attains when it is in contact with the boiling liquid
and free to escape into the atmosphere; or, in other words,
when it has a pressure or tension equal to that of the sur-
rounding atmosphere. If this pressure is increased by con- 24/1
fining the vapor or by rise in the atmospheric pressure, then
the temperature of the vapor and of the boiling liquid
will be higher; if the pressure is decreased by removal of
the vapor or by fall in the atmospheric pressure, the tem-
perature will be lower. For complete definition, therefore,
the pressure of the vapor, as well as the temperature, should

be specified, and the normal atmospheric pressure at the sea level—that is, 760 millimeters or 29.92 inches—is chosen as the standard pressure. The ordinary variations of the atmospheric pressure, however, have so small effect on the boiling point that the variation may for many purposes be ignored. A change of 27 millimeters (or 1.06 inches) in barometric pressure, or of about 1,000 feet in elevation, makes a difference of 1° C. in the boiling point. Thus water, boiling at 100° C. at sea level, boils at 85° C. on the top of Mont Blanc.

The facts that increase of pressure raises this temperature, and that decrease of pressure lowers the same, find many practical applications. Thus in extracting gelatine from bones, the solvent power of the water is increased by boiling under pressure; and in the refining of sugar the concentration of the sirup is greatly facilitated by evaporation under diminished pressure.

The boiling point has been defined, in accordance with scientific usage, as the temperature of the vapor. Yet the term is also used, even in scientific literature, to designate the temperature of the boiling liquid. This is unfortunate, since it is important to discriminate between the two, for the temperature of the liquid is often higher than that of the vapor. Various circumstances cause this. Whatever 24/2 tends to hinder the formation and escape of the bubbles of vapor tends to raise the temperature of the liquid above that of the vapor; conversely, whatever tends to facilitate the same, tends to make the temperature of the liquid the same as that of the vapor. Thus, water boils more readily in an iron vessel with rough surface than in a glass one with smooth surface. Indeed, in a glass vessel, whose inner surface has been very thoroughly cleaned, water may be raised to a temperature considerably above 100° C. In this condition a grain of sand or a fragment of glass dropped in, or a stirring rod inserted, may cause sudden and violent boiling. This phenomenon of irregular boiling, commonly called in the laboratory *bumping*, is often very annoying,

and various expedients are used to prevent it, such as constant stirring, or fragments of broken glass, or pumice, or platinum foil. Thus also the presence of dissolved air or other gas tends to facilitate boiling. On the other hand, 24/4 the presence of non-volatile substances in solution tends to raise the temperature of the boiling solution as compared with that of the pure solvent; this fact has important quantitative relations, which will be considered in Chapter V.

5. Definitions and Classifications

Some branches of chemistry.—It is suitable to introduce at this point some additional statements and definitions which do not call for special experimental illustration, although it is not to be expected that the full significance of these statements will be understood at this stage of the course. From what has been already presented, it may be seen that the subject-matter of our study has a twofold aspect. We 26 may give attention primarily to the description and identification and classification of definite chemical substances, and this may be called *static chemistry ;* or, on the other hand, we may give chief consideration to the changes of substances as changes, and this is the aim of *dynamic chemistry.* Of the first division are the subjects *qualitative analysis* and *quantitative analysis.* The former consists of systematic methods for the identification and recognition of substances; the latter, of methods for determining the quantities of substances. Analysis is *ultimate* when it is concerned with the qualitative or quantitative determination of elementary constituents; and *proximate* when it is concerned with constituents other than elementary.

In *dynamic chemistry* we have to consider such subjects as the factors, products, laws, agency, energetics, etc., of chemical change. For this last phrase the more technical one, chemical *reaction* or *interaction*, is commonly used. The *factors* are those substances in presence before the

change takes place; the *products*, those present after the change. The factors and the products considered collectively may be conveniently designated as the *system* undergoing change.

27   Elements and compounds defined.—All substances may be classified as *elements* or as *compounds*. An *elementary* substance is one from a given weight of which no other substance has been obtained less in weight than the original. Examples: sulphur, iron, zinc, iodine. A *compound* substance is one from a given weight of which other substances have been obtained, each less in weight than the original. Examples: sulphur dioxide, iron sulphide (Exp. $13/_2$ a), zinc sulphide, lead iodide (Exp. $15/_1$), magnesium, zinc, and lead oxides (Exps. $15/_2$, $15/_3$, and $15/_4$), lead nitrate (Exp. $16/_1$), zinc nitrate (Exp. $16/_2$).

28   It is important to distinguish between a *chemical compound* and a *mechanical mixture*. The first is homogeneous, and has properties of its own, distinct from those of its constituents; the second is not homogeneous, and shows only the properties of its components. Thus the powdered zinc and sulphur in your experiment (Exp. $13/_1$), before the application of heat, is a mechanical mixture, showing only the properties of the zinc and of the sulphur. A microscope distinguishes the different color of the zinc and sulphur particles. Water, dissolving neither, separates them more or less completely by difference in specific gravity. Carbon disulphide dissolves the sulphur and leaves the zinc, while hydrochloric acid dissolves the zinc and leaves the sulphur. But the product of the chemical change—that is, the zinc sulphide—has its own properties, distinct from those of zinc and those of sulphur.

29   It is customary to divide the elements into the *metals* and those which are not metals, that is, the *non-metals*, and to consider the two classes separately. This classification has largely lost its original significance and importance, however, and it is preferred, in this presentation, to

make the classification a secondary matter, and to use the term *metal* rather in the ordinary non-technical sense, implying those properties associated in familiar observation with substances like iron, copper, gold, and silver. But special importance is attached to the question concerning each element whether its combination with oxygen produces a base-forming or an acid-forming substance. The elementary substances in alphabetical list are given in Table X, No. 643. They number seventy-four, and to this comparatively small number of constituent substances all known forms of matter are reducible.

Compounds classified.—Three groups of compounds may **30** be defined now; they are important, although they do not by any means include all compounds. These are the *acids*, the *bases*, and the *salts*. The *acids* are substances contain- **30/1** ing hydrogen as a constituent, which hydrogen is replaceable by a metal, the product being a salt. When soluble in water, as most of them are, they are sour, change blue litmus to red, combine with bases to form salts, and in concentrated form are often very corrosive. Examples: hydrochloric, nitric, and sulphuric acids. A *base* is a substance **30/2** containing oxygen, often hydrogen also, and always a constituent other than these two which in the most common bases is a metal. When soluble in water, they are generally slimy to the touch, bitter, corrosive, change red litmus to blue, and combine with acids to form salts. Examples: ammonium hydroxide, sodium hydroxide, lime, that is, calcium oxide, and magnesium, zinc, and lead oxides. The *salts* are substances formed either by the replacement of **30/3** the hydrogen of an acid by a metal, or by the combination of an acid and a base. The peculiar properties of the acid and the base disappear in the salt, or are *neutralized*, sometimes completely, sometimes only in part. When they are neutralized exactly, so that the salt has no action on lit- **30/4** mus, it is said to be *neutral*. Examples: ammonium chloride, copper sulphate, zinc sulphate, lead nitrate. When

all the replaceable hydrogen of the acid is completely and
30/5 exactly replaced by its equivalent of metal, or basic con-
stituent, the salt is said to be *normal*. A normal salt may
have neutral, acid, or basic reaction on litmus; thus, ammo-
nium chloride is normal and neutral, alum is normal and
has acid reaction, sodium carbonate is normal and has basic
reaction. When a salt contains more than the normal
30/6 equivalent of acid, it is said to be an *acid* salt; such are
sodium acid carbonate, and acid sulphate. When it con-
tains more than the normal equivalent of base, it is said to
be a basic salt; such is the basic lead acetate.

31   **Reactions classified.**—Chemical reactions may be classi-
fied, in part only, as *analytic*, *synthetic*, and *metathetic*, or
mixed : *analytic*, when they change compounds into their
constituents; *synthetic*, when they change constituents into
compounds; and *metathetic*, when they involve both analy-
sis and synthesis, or the exchange of constituents. Thus
the conversion of iron and sulphur into iron sulphide is
purely synthetic ; of iron sulphide into iron and sulphur is
analytic ; while the action of hydrochloric acid on iron sul-
phide is metathetic, since the hydrogen and the chlorine of
the first and the iron and the sulphur of the second are
separated, and then the hydrogen and the sulphur combine,
also the iron and the chlorine. When a constituent of a
compound is caused to leave it, and another substance
appears as constituent in its stead, the process is called
substitution (see Exps. 17, etc.).

32   **Conclusion.**—The leading idea of this chapter is the fact
of chemical change—that is, the transformation of sub-
stances, involving the disappearance of some, and, depend-
ent upon this, the appearance of others. This has been
called change in identity. Along with this have been pre-
sented some definitions and classifications. And in this
connection it is interesting and instructive again to note
that the application of these to natural phenomena is often
unsuccessful. Thus it seems a simple matter to define

chemical changes as has been done; nevertheless changes are not infrequently encountered, of which it is impossible to decide whether they are chemical or not, because it is impossible to determine whether or not there is a distinctly new substance produced.   So also with regard to acids and bases : some substances act in one compound as acid and in another as base, and in some instances there seems as good reason to call it the one as the other.   None the less, we may make profitable use of such definitions and classifications; and at the same time, we do well to bear in mind the fact that nature is not limited by the boundaries of man's thought.

CHAPTER II

THE FUNDAMENTAL QUANTITATIVE LAWS OF CHEMICAL CHANGE

1. The Law of Persistence of Mass

34 HAVING now acquired a notion of the method of identifying and differentiating substances, and also of the remarkable transformations which a system of substances may undergo by which other substances are produced, differing entirely from the original in properties, we pass to a closer study of the peculiar quantitative characteristics of these chemical changes. And the most fundamental fact to be learned is, that by these changes the quantity of matter—that is, the mass of the system—is neither increased nor diminished. That this is true, does not by any means appear upon the face of things. Numerous experiences of everyday occurrence can be cited which would seem to prove that the reverse is true. Thus in the burning of wood, or of coal, or of a candle, one would conclude from appearances, as people did for many years, that matter is destroyed, or its quantity diminished. If we drop a piece of marble into hydrochloric acid, the marble slowly disappears. On the other hand, in seeing mercury sulphocyanate burn, one might suppose that the quantity of matter is largely increased. If, however, it is burned on the

34/1 balance, we see at once that the first supposition is wrong; that, although it has increased much in volume, the residue which is left on the balance after burning actually weighs less than the original material; and, if we burn a weighed

34/2 taper and collect and weigh the products of combustion,

we find that the products weigh more than the taper consumed.   Likewise, if we weigh the lump of marble and the **34/5**
acid before bringing them together and afterward, we
learn that loss of weight accompanies the disappearance of
the marble.   What is the explanation of these apparent
contradictions?

To answer this question we must investigate still further
beyond appearances.   We note that the disappearance of
the marble is also accompanied by effervescence.   This implies the liberation of a gas, the escape of which must cause
loss in weight.   We operate so as to retain the gas, and we
find neither loss nor gain in weight.   Likewise we may
learn that when the mercury sulphocyanate and the taper
burn, there is combination of the oxygen of the air, an
invisible gas, with the material of the combustible; and
that other gases are produced, also invisible, which by
escaping cause loss of weight; and, furthermore, that these
gaseous products, in the case of the taper, weigh more than
the taper consumed by just the weight of the oxygen which
has entered into combination.   The error of the earlier
conclusions, therefore, has come from overlooking some
of the substances involved in the change.   It is only
by taking them all into account that the truth has been
reached.

This great law is known as **The Indestructibility of Mat-** **34/6**
ter, or, better, as **The Persistence** * **or Conservation of Mass.**
It may be stated as follows:

*In any system of substances undergoing chemical change
the mass of the entire system remains constant, or the
total mass of the factors is equal to the total mass of the
products.*

This law is found to hold true throughout the whole **34/7**
range of experience, absolutely without exception; but that

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* " Persistence" is preferred to " Conservation," following the suggestion of Herbert Spencer in " First Principles."

it is based solely on experimental observation, and is not by
any means axiomatic, should not be forgotten.

34/8   It was not discovered until the balance was used to give
its evidence. And this was done in the main by Lavoisier,
a French chemist, in a series of investigations, extending
from 1770 to 1780, which showed the error of previous con-
ceptions, and which are regarded as the beginning of modern
chemistry.

34/9   This law has its parallel in that other great generaliza-
tion of more recent discovery, which lies at the founda-
tion of physical science, viz.: **The Law of the Conserva-
tion or Persistence of Energy,** which is that *in any system
of bodies, mutually interacting, the total energy of the
system remains constant.*

2. The Law of Fixed or Definite Proportions

37   Analysis of your experiment with ammonium hydroxide
and hydrochloric acid (No. 37) shows, within the limit of
accuracy attainable in the given conditions, that the masses
of these two substances which combine to form the salt,
ammonium chloride, bear a ratio to each other which is
constant in the three parts of the experiment; that an ex-
cess of either constituent above this ratio has no effect
upon the quantity of salt obtained nor upon its properties.
In other words, the three portions of salt obtained are dif-
ferent samples of the same definite substance and contain
the same relative quantities of the constituents, ammonium
hydroxide and hydrochloric acid.

37/4   The fact here illustrated is found to be a general one,
and to bear the test of the most refined experimental
methods without established exception. It is formulated
in **The Law of Fixed Proportions,** which may be thus stated:

37/5   *Any sample of a definite chemical substance, not elementary,
is composed of the same constituents, combined in the same
relative quantities, as any other sample of the same substance.*
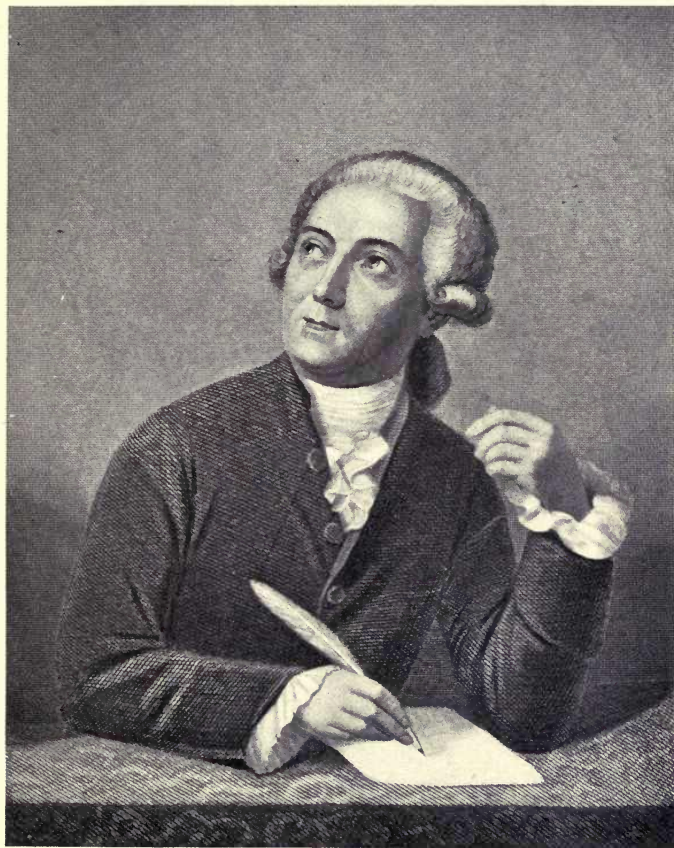
ANTOINE LAURENT LAVOISIER

B. Paris, 1743.   D. on the scaffold, 1794.

(See Nos. 34/$_8$, 235, 259, 306, 388.)

The conception of the fixity of ratios was in the minds **37/6** of chemists more than one hundred years ago. Bergmann was apparently guided by it, and Lavoisier distinctly formulated it, but its truth was not admitted without dispute. It was called in question in 1799 by Berthollet, a famous French chemist. This led to a long discussion, one of the most remarkable in the history of the science, between him and another French chemist, named Proust, who undertook the defense of the law. The ideas of the latter prevailed, and, by 1806, the truth of the proposition was generally admitted; although even in late years there have appeared suggestions that the law may be subject to variations within very narrow limits. In view of this history and of the nature of the law itself, the same degree of absoluteness should not be claimed for it as for the first law.

It is to be noted that the Law of Fixed Proportions **37/7** affirms the intimate relation between properties and composition. With identity of properties there is identity of composition. It does not, however, follow from this, nor is it indeed true, that with identity of composition there is identity of properties. There are many substances not identical, which are nevertheless composed of the same constituents combined in the same quantitative ratio.

To the Law of Fixed Proportions may be given an **37/8** **Alternative Statement,** somewhat broader and more suggestive of the dynamic conception, thus:

In any system of substances undergoing chemical change, the active masses—that is, the quantities actually taking part in the change, both of factors and of products—bear a fixed ratio to each other, always the same for a specified change.

3. The Law of Multiple Proportions

The third characteristic of chemical change is perhaps **40** even more striking than the two already studied, and is of very great significance. It was noted by Proust, and still

earlier by Richter, that some substances combine in more than one ratio, producing distinctly different substances. They failed, however, to note the multiple relation of the varying quantities. This was due, perhaps, in part to the inaccuracy of their quantitative determinations. It was left to Dalton, a teacher and chemist living in Manchester, England, to discover this important relation and to announce it about the year 1804.

The law is illustrated in your experiments with mercury and iodine (Exps. 40, etc.), wherein it is seen that these substances combine in two different ratios, producing two distinctly different substances, and that for the same weight of mercury the weight of iodine in one is just twice that in the other.

The general fact is known as **The Law of Multiple Proportions,** and may be stated thus :

If two substances combine in more than one ratio, forming distinctly different products, and if in such cases the quantity of one constituent is reckoned as constant, then the varying quantities of the other constituent are in the ratio of small whole numbers.

40/6   It was the discovery of this law, based, it is true, on very few observed instances, that led Dalton to the invention of the atomic theory in its modern form—a theory which in importance is second to none in the science of chemistry.

40/7   NOTE.—The law holds without exception, although there are many instances in the so-called organic substances, compounds of carbon with other elements, in which the relation seems less simple than is stated in the law, but they do not constitute valid exceptions to the law for reasons which would hardly be understood at this stage of the course.

40/8   The multiple relation holds for quantities measured by volume as well as by weight, if the substances are in the gaseous condition.

4. The Law of Equivalent Proportions *

It has been seen in your experiments, Nos. $41/_1$ and $41/_2$, **41** that 24 grams of magnesium and 65 grams of zinc combine respectively with 16 grams of oxygen approximately. Defined with the utmost accuracy, the statement is that 24.1 grams of magnesium and 64.91 grams of zinc combine respectively with 15.88 grams of oxygen. It is also a fact, although not shown in your experiments, that these same masses of magnesium and zinc combine respectively with equal quantities of chlorine, namely, (2×35.18) grams, and with equal quantities of iodine, namely, (2×125.89) grams.

Then in your experiments, Nos. $41/_3$ and $41/_4$, it is seen that these masses likewise displace equal quantities of hydrogen from an acid. This value, most accurately determined, is 2 grams. Now, magnesium and zinc do not combine with each other, but 2 grams of hydrogen exactly combine with 15.88 grams of oxygen in the formation of water; and one gram of hydrogen combines exactly with 35.18 grams of chlorine, and with 125.89 grams of iodine.

Still another phase of this phenomenon is seen in the **41/6** following facts: 31.83 grams of sulphur combine with 64.91 grams of zinc; also, 15.88 grams of oxygen with 64.91 grams of zinc; and sulphur and oxygen combine with each other in the ratio of $31.83 : (2 \times 15.88)$ in sulphur dioxide and $31.83 : (3 \times 15.88)$ in sulphur trioxide.

Generalization upon the many facts of this nature gives

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* Inasmuch as the experimental study of this law involves the measurement of gas-volume, the instructor may prefer to introduce the laws of Boyle and of Charles, Chapter IV, at this point. The writer prefers to give them simply as arbitrary rules and to study them later, rather than to interrupt the logical development of this chapter.

41/7 The Law of Equivalent Proportions, to which there seems to be no exception; it may be stated thus:

The masses of two or more substances, A, B, C, etc., which combine respectively with a constant mass of another substance, M, are also the masses or bear the relation of small multiples to the masses of A, B, C, etc., which may combine respectively with a constant mass of any other substance, X, or which may be chemically substituted respectively for a constant mass of a substance, X, or which may combine with each other.

We may conceive that the masses of two substances, A and B, produce equal chemical effect when they combine respectively with a constant mass of the substance, X; likewise when they displace a constant mass of the constituent, C, from the compound, C D; also when they combine with each other to form the compound, A B. By means of this conception the law may be given a more general expression **41/8** in **An Alternative Statement,** thus:

Those active masses of substances which produce equal chemical effect in a given reaction are also the active masses or bear the relation of small multiples to the active masses of the same substances which produce equal effect in any other reaction in which they take part.

41/9 The first notion of the remarkable facts generalized in the fourth law, without by any means a conception of their full extent or of their significance, is credited by some to a German chemist, Richter, and to the year 1792, and by others to Wenzel, and the earlier date, 1777.

Corollaries.—The following important corollaries are deducible from the fourth law, taken in connection with those which precede:

42 COROLLARY I.—*It is possible to determine by experiment what mass of every elementary substance combines with one gram of hydrogen (the lightest substance specifically and chemically) or with that quantity of some other substance which, in its turn, combines with one gram of hydrogen*

(*practically 7.94 grams of oxygen, or 35.18 grams of chlo-
rine*) ; *or, what mass displaces one gram of hydrogen from
some specified compound. And, moreover, the constituent
masses of the elements in any compound, and their active
masses in any reaction, stand in the ratio of these quan-
tities or of multiples of the same by a whole number.*

Definition.—These fundamental quantities, specified in **43**
Corollary I, are called the *equivalent weights* or *equivalent
masses* of the elements. Now, many of the elements com-
bine with hydrogen or with oxygen, or with chlorine in more
than one ratio. These substances would have, therefore,
two or more values which would answer the definition of
equivalent weight. But since the relation of multiples
holds between these values, as expressed in Law 3, the fact
that there may be more than one value does not interfere
with the truth of Corollary I.

Great significance, both practical and theoretic, attaches **44**
to the equivalent weights and to the facts formulated in
this corollary. And the whole system of expressing mass
relations in chemical phenomena is based upon the use of
the equivalent weight, or of a multiple of the same, as a
chemical unit, peculiar to each element, and upon the ex-
pression of the relative active mass in terms of this unit,
with a coefficient which is always a whole number. That
such a system is possible, is clearly a consequence of the
foregoing laws. That one equivalent rather than another
is used, when two or more are possible, or that a multiple
instead of the equivalent itself is used as the basal unit, is
a matter of choice, determined conventionally by the applica-
tion of certain principles or of certain theories. For the
reasons which are presented in detail in Chapter V, the
equivalent weights of certain of the elements have been
multiplied by a small whole number, two, three, four or five,
and the values thus obtained together with those of the
equivalent weights which are left unmodified, all of them
determined with the utmost available accuracy, constitute

the elementary *combining weights*, which are made the basal units, just referred to, for expressing the quantitative mass relations in chemical phenomena.

The elements with their equivalent weights, the factors, and the combining weights are given in Table XI, No. 644, in natural order—i. e., in the order of increasing combining weights.

45   COROLLARY II.—*It is evident that the combining mass of a compound must be the sum of its elementary constituent combining masses.*

For example: Using round numbers simply, the combining weight of water is 18 grams, since it contains hydrogen and oxygen in the ratio of 2 grams to 16 grams—that is, two combining weights of the former to one combining weight of the latter; of ammonia is 17 grams, since it contains nitrogen and hydrogen in the ratio of 14 grams to 3 grams —that is, one combining weight to three combining weights; of carbon dioxide is 44 grams, since it contains carbon and oxygen in the ratio of 12 to 32—that is, one combining weight to two combining weights.

46   COROLLARY III.—*It is possible, therefore, to represent the relative active masses of all substances, in any reaction whatsoever, as multiples by whole numbers of their respective combining masses.*

5. The Law of Gas-volumetric Proportions

47   The experiments (No. 47, etc.) with nitrogen dioxide and oxygen, designed to illustrate this law, are only partly satisfactory, since the volume of the product can not be measured in the conditions of the experiment, the substance, nitrogen tetroxide, being soluble in water. Additional illustrations are found in the following facts :

1 gas-vol. of hydrogen and 1 gas-vol. of chlorine (sum = 2) form 2 gas-vols. of hydrochloric acid.

2 gas-vols. of hydrogen and 1 gas-vol. of oxygen (sum = 3) form 2 gas-vols. of water.

3 gas-vols. of hydrogen and 1 gas-vol. of nitrogen (sum $=4$) form 2 gas-vols. of ammonia.

In these is revealed the surprising but none the less unmistakable fact, based solely on experimental observation, that the gas-volume of a compound is not always equal to the sum of its constituent volumes, but may be less.

Facts of this nature are generalized into **The Law of Gas-volumetric Proportions** as follows:

If the constituents are gaseous or volatile their combining volumes, as gases, are in the ratio of small whole numbers, and the sum of these volumes stands in simple relation to the volume of the resulting compound, if the latter is gaseous or volatile. In general, the compound occupies two unit gas-volumes.

Note carefully that the law is applicable only to gas- **47/5** volumes; no such relations hold between combining volumes other than gaseous.

The accuracy of the law is of course limited by the ac- **47/6** curacy in the measurement of gas-volumes. There has been much dispute as to the generality of the rule that the compound occupies relatively two unit volumes. In several instances its volume is undoubtedly larger, but it has been proved with much ingenuity that these exceptional volumes are due to the decomposition (dissociation) of the compounds in the conditions of observation, so that the observed volume is really the volume of a mixture of the constituents, and not of the compound solely.

The discovery of the law is due mainly to Gay-Lussac, **47/7** who with Humboldt determined in 1805 the gas-volumetric composition of water, and subsequently extended his investigations to other substances. The large significance of this law in the interpretation of chemical phenomena was not realized, however, until a considerably later date.

TABLE I

49   As aid to a clearer understanding of these laws, the illustrations which have occurred in the experiments, and some additional ones, are tabulated as follows:

1 gram of hydrogen (H) combines with

> 35.2 grams of chlorine (Cl), forming 36.2 grams of hydrochloric acid (HCl).
> 79.3 grams of bromine (Br), forming 80.3 grams of hydrobromic acid (HBr).
> 125.9 grams of iodine (I), forming 126.9 grams of hydriodic acid (HI).

2 grams of hydrogen combine with

> 15.9 grams of oxygen (O), forming 17.9 grams of water (H_2O).
> 31.8 grams of sulphur (S), forming 33.8 grams of hydrosulphuric acid (H_2S).

3 grams of hydrogen combine with

> 13.9 grams of nitrogen (N), forming 16.9 grams of ammonia (NH_3).

4 grams of hydrogen combine with

> 11.9 grams of carbon (C), forming 15.9 grams of methane (marsh gas) (CH_4).

13.9 grams of nitrogen (N) combine with

> 7.94 grams of oxygen (O), forming 21.8 grams of nitrous oxide (nitrogen monoxide) (N_2O).
> 15.9 grams of oxygen (O), forming 29.8 grams of nitric oxide (nitrogen dioxide) (NO).
> 23.8 grams of oxygen (O), forming 37.7 grams of nitrogen trioxide (N_2O_3).
> 31.8 grams of oxygen (O), forming 45.7 grams of nitrogen tetroxide (N_2O_4).
> 39.7 grams of oxygen (O), forming 53.6 grams of nitrogen pentoxide (N_2O_5).

198.5 grams of mercury (Hg) combine with

> 125.9 grams of iodine (I), forming 324.4 grams of mercurous iodide (HgI).
> 251.8 grams of iodine (I), forming 450.3 grams of mercuric iodide (HgI_2).

15.9 grams of oxygen (O) combine with

> 24.1 grams of magnesium (Mg), forming 40.0 grams of magnesium oxide (MgO).
>
> 55.6 grams of iron (Fe), forming 71.5 grams of ferrous oxide (FeO).
>
> 63.1 grams of copper (Cu), forming 79.0 grams of copper oxide (CuO).
>
> 64.9 grams of zinc (Zn), forming 80.8 grams of zinc oxide (ZnO).
>
> 198.5 grams of mercury (Hg), forming 214.4 grams of mercuric oxide (HgO).
>
> 205.3 grams of lead (Pb), forming 221.2 grams of lead oxide (PbO).

31.8 grams of sulphur (S) combine with

> 24.1 grams of magnesium (Mg), forming 55.9 grams of magnesium sulphide (MgS).
>
> 55.6 grams of iron (Fe), forming 87.4 grams of ferrous sulphide (FeS).
>
> 63.1 grams of copper (Cu), forming 94.9 grams of copper sulphide (CuS).
>
> 64.9 grams of zinc (Zn), forming 96.7 grams of zinc sulphide (ZnS).
>
> 198.5 grams of mercury (Hg), forming 230.3 grams of mercuric sulphide (HgS).
>
> 205.3 grams of lead (Pb), forming 237.1 grams of lead sulphide (PbS).

31.8 grams of sulphur (S) combine with

> 15.9×2 grams of oxygen, forming 63.6 grams of sulphur dioxide (SO_2).
>
> 15.9×3 grams of oxygen, forming 79.5 grams of sulphur trioxide (SO_3).

2 grams of hydrogen are displaced from hydrochloric acid by

> 24.1 grams of magnesium, forming magnesium chloride ($MgCl_2$).
>
> 55.6 grams of iron, forming ferrous chloride ($FeCl_2$).
>
> 63.1 grams of copper, forming cupric chloride ($CuCl_2$).
>
> 64.9 grams of zinc, forming zinc chloride ($ZnCl_2$).
>
> 198.5 grams of mercury, forming mercuric chloride ($HgCl_2$).
>
> 205.3 grams of lead, forming lead chloride ($PbCl_2$).

36.2 grams of hydrochloric acid (HCl) combine with

> 16.9 grams of ammonia (NH_3), forming 53.1 grams of ammonium chloride (NH_4Cl).

63.6 grams of SO_2 combine with

> 15.9 grams of O, forming 79.5 grams of sulphur trioxide (SO_3).

79.5 grams of SO_3 combine with
> 17.9 grams of H_2O, forming 97.4 grams of sulphuric acid (H_2SO_4).

59.6 grams of NO combine with
> 31.8 grams of O, forming 91.4 grams of nitrogen tetroxide (N_2O_4).

27.8 grams of CO combine with
> 15.9 grams of O, forming 43.7 grams of carbon dioxide (CO_2).

49/1   In the following, the volumes are gaseous:

1 liter of hydrogen (H) combines with
> 1 liter of chlorine (Cl), forming 2 liters of hydrochloric acid (HCl).
> 1 liter of bromine (Br), forming 2 liters of hydrobromic acid (HBr).
> 1 liter of iodine (I), forming 2 liters of hydriodic acid (HI).

2 liters of hydrogen combine with
> 1 liter of oxygen, forming 2 liters of water (vapor) (H_2O).

3 liters of hydrogen combine with
> 1 liter of nitrogen, forming 2 liters of ammonia (NH_3).

1 liter of sulphur (vapor) combines with
> 2 liters of oxygen, forming 2 liters of sulphur dioxide (SO_2).
> 3 liters of oxygen, forming 2 liters of sulphur trioxide (SO_3).

2 liters of nitrogen combine with
> 1 liter of oxygen, forming 2 liters of nitrous oxide (N_2O).

1 liter of nitrogen combines with
> 1 liter of oxygen, forming 2 liters of nitric oxide (NO).
> 2 liters of oxygen, forming 2 liters of nitrogen peroxide (NO_2).

2 liters of sulphur dioxide (SO_2) combine with
> 1 liter of oxygen, forming 2 liters of sulphur trioxide (SO_3).

4 liters of nitric oxide (NO) combine with
> 2 liters of oxygen, forming 2 liters of nitrogen tetroxide (N_2O_4).

2 liters of carbon monoxide (CO) combine with
> 1 liter of oxygen, forming 2 liters of carbon dioxide (CO_2).

6. The Law of Persistence, or Conservation of Energy, applied to Chemical Phenomena

Heat Disturbance in Chemical Reactions

Chemical changes are generally accompanied by changes **50** in energy. You have observed in your experiments several instances in which they have been accompanied by the liberation of heat, sometimes sufficient to raise the mass to incandescence—that is, to a red or white heat, as in the combinations of sulphur with iron and with zinc; sometimes, less noticeable, as in the action of mercury and iodine; and sometimes, still less marked, as in the reaction of ammonium hydroxide and hydrochloric acid, and in the action of the latter on magnesium and on zinc. Likewise the reaction between nitric oxide and oxygen liberates heat, although, in the conditions of your experiment, you could not easily observe it.

Now, heat is one of the kinds of energy, and the immediate agent which causes chemical change is another kind. Energy has been defined as that which brings about changes, or, in the more common wording, it is the power of doing work. **The Law of the Persistence of Energy** affirms * (compare 34/9, Part I) that, *although the various kinds of energy may be transformed from one kind into another, the total energy can not be thereby increased nor diminished.* Inasmuch, therefore, as heat, not before evident, appears when iron and sulphur become iron sulphide, and when mercury and iodine become mercuric iodide, it must be that iron sulphide and mercuric iodide as compared with their constituents have lost at least as much energy as is equivalent to the heat produced. The energy which is lost is the chemical energy or *chemism,* as it is sometimes called. It **51**

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* This law was announced by J. A. Mayer in 1842, greatly developed by Helmholtz in 1847, and experimentally tested by Joule in 1850.

may be that the chemical energy which is lost does not appear entirely as heat; nevertheless, the quantity of heat liberated is constant for a specified change under specified conditions.

52   Again, it follows from this great law that, in order to reverse this change—that is, to produce from iron sulphide and mercuric iodide, iron and sulphur, and mercury and iodine—the quantity of energy lost in the first change must be restored to the system in one form or another.

53   The quantity of heat liberated in the original reactions is called the *heat of formation* of iron sulphide and of mercuric iodide from their constituents respectively. But heat is not always liberated in the formation of compounds; it is sometimes absorbed—that is, some substances have a negative heat of formation; they possess more energy than their constituents, and consequently liberate energy in decompos-

54   ing. Reactions which liberate heat and compounds whose heat of formation is positive are said to be *exothermic*; those which absorb heat and those which have a negative heat of formation are called *endothermic*.

The measurement of the heat liberated or absorbed in chemical changes becomes therefore an important item for investigation, and many extremely interesting conclusions have been reached by the study of these phenomena. The possibility of such measurement for reactions which are directly and quickly realizable can be easily understood; and the application of a corollary of the law of persistence of energy makes it possible to determine these thermal values for reactions which can not be brought about in conditions suitable for heat measurement, and, in some instances, for reactions which can not be brought about at all.

55   This corollary as applied to chemical phenomena is known as **The Law of Constant Heat Summation.** It was formulated by Hess in 1840, as follows: *The quantity of heat liberated or absorbed by a system of substances undergoing chemical change is dependent on the initial and final states of the sys-*

*tem, and is not affected by differences in the intermediate
states through which the system may pass.*

An illustration from the reactions which you have studied
will make this clear : 16.9 grams of ammonia combine with
36.2 grams of hydrochloric acid, forming 53.1 grams of
ammonium chloride, a soluble salt. Now let us suppose
that we start with ammonia and hydrochloric acid as gases
at the ordinary temperature, and end with the salt dissolved
in water at the same temperature. The system may be
passed from this initial state to this final state in two dif-
ferent ways : the two gases may be directly combined, form-
ing the solid salt, and then this may be dissolved in the
water ; or, the gases may be separately dissolved in water
and the two solutions mixed, the salt being formed in solu-
tion. The law affirms that the heat disturbance, in passing
from this initial to this final state, is the same, whichever
method of reaching the final state is used. The law is ex-
perimentally verified by measuring the heat of solution of
16.9 grams of ammonia gas (8,400 calories) and of 36.2 grams
of hydrochloric acid gas (17,300 calories), and the heat of
neutralization of the two solutions (12,300 calories), and
summing these three quantities (= 38,000 calories) ; also,
the heat of formation of 53.1 grams of solid ammonium
chloride from the two gases (42,100 calories) and the heat
of solution of the salt (— 3,900 calories) and summing these
two quantities (= 38,200 calories). The two sums are found
equal within the limits of experimental error.

Another method of application is seen in the determina-
tion of the heat of formation of 15.9 grams of methane
from its constituents, namely, 11.9 grams of carbon and
4 grams of hydrogen ; although these elements can not
be made to combine directly into this compound. Methane
is a combustible gas ; 15.9 grams in burning produce 43.66
grams of carbon dioxide and 35.76 grams of water ; and the
heat liberated in this reaction is found to be 212,000 calories.
Furthermore, 11.9 grams of carbon in burning alone liberate

97,000 calories; and 4 grams of hydrogen in burning alone liberate 136,800 calories. Now, starting with 11.9 grams of carbon and 4 grams of hydrogen, we may burn them separately with the requisite quantity of oxygen and convert them into 43.66 grams of carbon dioxide and 35.76 grams of water with the liberation of $97,000 + 136,800 = 233,800$ calories. Or, starting with these same quantities, we may conceive them converted into 15.9 grams of methane, the formation heat of which, x, is unknown, and then the latter substance burned with the liberation of 212,000 calories. Now, by the law, since the initial and final states are the same, $x + 212,000 = 233,800$; hence $x = 21,800$ calories.

56   One gram of hydrogen in burning to liquid water liberates 34,200 calories, which is more heat than is liberated by the combustion of an equal weight of any other substance. The bottleful of gas which you collected in your experiments with magnesium and zinc weighed 0.2 of a gram. This, if burned, would yield enough heat to raise 2.7 such bottlefuls of water 1°, or to raise 68 grams of water (nearly 2.5 ounces) from 0° to 100°.

57   The following are the formation heats of some of the substances which have been used in your study:

Water,	H_2O	=	68,400	calories
Sulphur dioxide,	SO_2	=	71,000	"
Carbon dioxide,	CO_2	=	97,000	"
Hydrogen sulphide,	H_2S	=	2,700	"
Mercuric iodide,	HgI_2	=	24,300	"
Mercurous iodide,	HgI	=	14,200	"
Magnesium oxide,	MgO	=	143,400	"
Zinc oxide,	ZnO	=	85,800	"

Examples of negative formation heat are:

Chlorine monoxide,	Cl_2O	=	− 17,800	calories
Nitrogen monoxide,	N_2O	=	− 18,000	"
Nitrogen tetroxide,	N_2O_4	=	− 2,600	"
Nitric oxide,	NO	=	− 21,600	"
Cyanogen,	$(CN)_2$	=	− 65,600	"
Acetylene,	C_2H_2	=	− 47,600	"

Endothermic substances often show great readiness to 58 react, and are easily decomposed, sometimes explosively so —e. g., chlorine monoxide and acetylene.

Chemical energy and electricity.—Chemical energy may 59 be transformed not only into heat, but also into electrical energy. You have observed that heat is liberated by the solution of zinc in hydrochloric acid. Now, if a sheet of zinc is partly immersed in a beaker of dilute acid, and a sheet of copper, or a carbon plate, neither being acted on by the acid, is likewise immersed in the same vessel, but separated from the zinc, and finally, if the ends
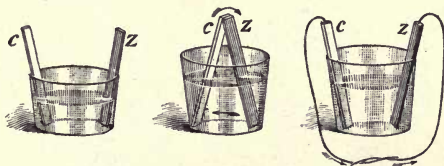
FIG. 1.—The galvanic cell—a zinc and a copper plate (*Z* and *C*) immersed in dilute acid.

not immersed be brought in contact outside the liquid, or connected by a metallic wire, the chemical energy set free by the solution of the zinc in the acid now appears, at least in part, not as heat but as the energy of the electric current. This constitutes one form of the galvanic battery, in all forms of which the electrical energy is due to the chemical changes taking place in the generating cell.

Indeed, it may be said that, of all the forms of energy, 60 the one which produces chemical change is the most familiar and the most intimately associated with human activities; at the same time it is perhaps the least understood. Not only are all those industrial applications of energy which involve the use of steam and fuel dependent on the energy of combustion, which is purely a chemical change, but, in

the animal organism, the heat, and the energy of muscle, nerve, and brain, are likewise derived from the chemical changes which the food and other substances undergo in the animal economy. [See Ostwald (Walker), " General Chemistry," page 209.]

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(See No. 37/₆.)

CHAPTER III

COMBINING WEIGHTS—NOTATION—EQUATIONS—STOICHIOMETRY—NOMENCLATURE

1. Combining Weights

THE combining weights of the elements have already **61** been defined (Nos. 43 and 44, Part I). They are multiples of the equivalent weights by a small whole number (one to five). These multiples may be regarded, for the present, as conventionally chosen in accordance with principles which will be explained in Chapter V. The relative active mass of an element as a constituent in any compound and as a factor in any reaction is represented as a multiple of the combining weight by a whole number. That this is possible is simply a consequence of the fundamental quantitative laws, studied in the last chapter. The system of combining weights, therefore, constitutes the basis for the quantitative expression of chemical phenomena. Later it will be seen that very important theoretical conceptions center about these values.

2. Notation

The System of Chemical Notation: **62**

(*a*) **For the elements.**—This consists simply in representing the element by a symbol—usually the first letter, sometimes accompanied by another, of its name; quantitatively the symbol represents the combining mass of the element in grams.

37

(*b*) **For compounds.**—This consists in representing the compound by a symbol or formula made up of the symbols of its elementary constituents, these being affected by integral coefficients such that multiplication of the elementary combining weight by the coefficient shall give products which· show the relative masses of the respective elements contained in the compound. The coefficient is written below the line and follows the symbol to which it belongs. If the coefficient is one, it is omitted altogether. A coefficient written on the line affects the symbols which follow it. Thus for hydrochloric acid the formula is HCl, since it contains hydrogen and chlorine as elementary constituents, and contains these in the ratio of one combining mass of hydrogen to one combining mass of chlorine—that is, 1 gram to 35.2 grams. The formula of water is H_2O, since it contains 2 grams of hydrogen to 15.9 grams of oxygen; of ammonium chloride is NH_4Cl, since it contains nitrogen, hydrogen, and chlorine in masses proportional respectively to 13.9 : 4 : 35.2.

62/1   It is clear that the formulas, H_2Cl_2, H_4O_2, and $N_2H_8Cl_2$ would represent the same relative quantities of the elements as those given above, and so with any set of coefficients which preserve the ratio of the first. It is customary to use the simplest set of coefficients, unless there is reason for using multiples of these. The considerations which determine the choice of these possible multiples are presented in Chapter V.

62/2   The combining weight of a compound becomes therefore the sum of its elementary constituent masses, as expressed by its formula. It is sometimes called the *formula weight.*

In the formulas of acids the H is usually placed first; in those of bases and of salts the symbol of the metal is usually placed first; in those of oxides the O is usually placed last.

PROBLEMS.—Calculate the relative quantities of the elementary constituents as expressed in the following formulas; also the combining

weights of the compounds: SO_2, FeS, ZnS, H_2S, $FeCl_2$, $FeCl_3$, $PbCl_2$, $CuSO_4$, $[Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O]$, $C_2H_4O_2$, C_2H_2, C_6H_6.

Reckon also the grams of the constituents contained in 100 grams of the compounds—that is, the percentage composition of the latter.

3. Equations

The chemical equation is an attempt to describe a **63** chemical reaction qualitatively and quantitatively in the concise form of an equation; in it, the symbols of the factors, separated by the sign $+$, are written on the left, and those of the products, similarly separated, on the right of the sign of equality ($=$), which is better interpreted by the word *become* or *produce* than by the word *equal*; the sign $+$ is interpreted by *and* or *mixed with*. When the symbols of the substances brought together are known, the first member is easily written; in order to write the second, it must be learned, originally of course by observation, exactly what substances are produced when the factors are brought together; but this depends upon conditions, as you have already had opportunity to observe, and of these the equation offers no means of expression. Thus the equation

$$Fe + S = FeS$$
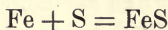
means that iron and sulphur mixed become iron sulphide, but this is not true unless the mixture be heated considerably above the ordinary temperature. Therefore the equation, even in its qualitative aspect, is defective, and only expresses those substances which, under certain conditions, not specified, are produced from the given factors. Yet even thus limited, the equation is useful in bringing quickly to the eye the relations as to composition between the factors and the products.

But the equation may be used as a means of express- **63/1** ing also quantitative relations by letting each symbol stand for a quantity of the substance named which is equal to the combining weight in grams, or in other units of

weight, and applying to it the coefficient which is neces-
sary to express the relative quantities actually taking part
in the reaction—the active masses, as they have been
called.   Thus the equation

$$Fe + S = FeS,$$
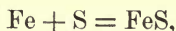
quantitatively interpreted, means that iron and sulphur
produce iron sulphide in the proportion of 55.6 grams, or
other parts by weight, of iron, to 31.8 of sulphur, to 87.4 of
iron sulphide.   And the equation

$$Zn + 2HCl = ZnCl_2 + 2H,$$
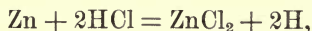
quantitatively interpreted, means that 64.9 grams of zinc
and (2×36.2) grams of hydrochloric acid produce 135.3
grams of zinc chloride and 2 grams of hydrogen.   Clearly,
then, before the equation can be used for quantitative
expression, the facts as to the relative quantities must be
ascertained.   This can be done originally only by observa-
tion, and often involves much labor and difficulty.   How-
ever, it may be assumed that the reaction as expressed by
the equation must be in accordance with the fundamental
laws of quantity just studied.   Thus by Law 1 there must
be represented on one side of the equation the same quan-
tity of each element as upon the other side—that is, the
equation must "balance."   Moreover, it is sometimes pos-
sible, when one has become familiar with a good many
reactions of the same kind, to surmise with some degree
of certainty what change will take place in given condi-
tions.   Nevertheless, the beginning student should care-
fully bear in mind that facts must be established before
equations are written ; and that, because an equation is
written, and written in accordance with the laws of
quantity, it does not follow that it represents an actual
reaction.

63/2   Again, the equation as described expresses nothing as
to the energy changes which always accompany the trans-

formations of matter. So far as the former consist of heat changes, they are expressed by a slight extension of the ordinary chemical equations. Thus:

$$Mg + O = MgO + 143,400 \text{ calories}$$
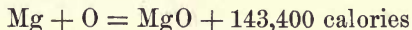
means that 24.1 grams of magnesium combine with 15.88 grams of oxygen, producing 39.98 grams of magnesium oxide and liberating 143,400 calories of heat energy.

And the equation

$$MgO = Mg + O - 143,400 \text{ calories}$$
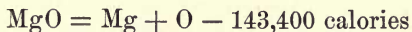
means that 39.98 grams of magnesium oxide, in decomposing into 24.1 grams of magnesium and 15.88 grams of oxygen, absorb the equivalent of 143,400 calories.

4. Stoichiometry

It will be readily understood that when the facts as to **64** relative quantities or active masses in a given reaction are known, they may be applied, under the quantitative laws and by purely arithmetical analysis, to ascertain the actual quantities involved in specified conditions. For example: Suppose the problem is to calculate how much hydrogen would be liberated by the action of 100 grams of zinc on hydrochloric acid. The chemical fact is that it takes 64.9 grams of zinc to liberate 2 grams of hydrogen (see equation in $63/_1$), and that the reaction always takes place in this proportion by Law 2; therefore by arithmetical analysis the proportion, $64.9 : 2 :: 100 : x$ gives the desired result. Such chemical facts will be most easily recalled, probably, in equation form; hence in solving problems of this kind **64/1** it is well first to write the equation for the reaction involved, then to give to this its quantitative interpretation and apply simple arithmetic. Calculation of this kind, based on the quantitative relations of reactions, is called *Stoichiometry* or *Chemical Arithmetic*.

5. Nomenclature

65   Chemical nomenclature is not thoroughly systematic. Some names, so far as compounds are concerned, give, with more or less system, some indication as to the composition and the relations of the substances; others have been arbitrarily assigned, perhaps before the chemical nature of the substances was known. Only a few general statements are here given; the rest may come gradually as acquaintance with substances is extended.

65/1   The elements in general combine with oxygen, and the resulting compounds are termed *oxides* (spelled also *oxids*). Examples: hydrogen oxide (commonly called water), zinc oxide, iron oxide, sulphur oxide.

The ending *ide* (*id*) is generally applied to the name of one of the constituents in a compound which contains but two; thus, *carbides*, *nitrides*, and *phosphides* contain respectively carbon, nitrogen, and phosphorus, with another element; *sulphides*, *chlorides*, *bromides*, and *iodides* contain sulphur, chlorine, bromine, and iodine with another element.

65/2   When there is more than one compound containing the same constituents they are distinguished sometimes by the endings *ous* and *ic*, as mercurous iodide (HgI), in which the mercury shows its *lower* combining power, and mercuric iodide (HgI_2), in which it shows its *higher* combining power; and sometimes by numerals as prefixes, as in carbon *mon*oxide (CO) and carbon *di*oxide (CO_2).

65/3   **Names of acids.**—Acids containing no oxygen are given the prefix *hydro* and the ending *ic*. Examples: hydrochloric, HCl, and hydrosulphuric, H_2S. Other peculiarities are illustrated in the following series:

*Hypo*chlor*ous* acid.................	$HClO$
Chlor*ous* acid.....................	$HClO_2$
Chlor*ic* acid..................... .	$HClO_3$
*Per*chlor*ic* acid.................	$HClO_4.$

Names of salts.—The salts of acids which contain no 65/4 oxygen are named by dropping the prefix *hydro* of the acid and changing the ending *ic* to *ide* (or *id*). Examples: zinc chloride, iron sulphide.

The ending *ic* in the names of acids which contain oxygen is changed to *ate* in naming their salts; and the ending *ous* in the acid to *ite* in the salt. Thus the sodium salts of the acid series above mentioned are named respectively sodium hypochlor*ite*, chlor*ite*, chlor*ate*, and *per*chlor*ate*.

Names of bases.—Bases which contain hydrogen and 65/5 oxygen and another constituent (usually a metal) are now commonly named *hydroxides* (or *ids*), although they were formerly, and by some are still, called *hydrates*. Examples: sodium hydroxide, $NaOH$; ammonium hydroxide, NH_4OH; and zinc hydroxide, $Zn(OH)_2$.

STOICHIOMETRIC PROBLEMS

1. How much sulphur will exactly combine with 75 grams of 65/6 iron?

2. How much zinc with 50 grams of sulphur?

3. How much zinc is needed to make 50 grams of zinc chloride $(ZnCl_2)$?

4. How much marble $(CaCO_3)$ must be used with hydrochloric acid to generate enough carbon dioxide (CO_2) to neutralize 50 grams of sodium hydroxide $(NaOH)$, forming sodium carbonate (Na_2CO_3)?

5. How much mercury must be added to 90 grams of mercuric iodide (HgI_2) to convert it into mercurous iodide (HgI)?

6. What volumes of carbon monoxide (CO) and of oxygen must be taken to produce by combination enough carbon dioxide (CO_2) to neutralize 10 grams of sodium hydroxide? One liter of oxygen weighs 1.43 grams; one liter of carbon monoxide weighs 1.25 grams.

7. How much magnesium is needed to generate with hydrochloric acid enough hydrogen to form by burning 10 grams of water?

8. Given: a sample of hydrogen containing nitrogen as impurity, and a sample of oxygen also containing nitrogen as impurity; to determine the percentage of impurity in each case. Measured volumes are caused to combine, forming water, liquid at ordinary temperature,

and the following observations are made, from which calculate the impurity:

Hydrogen taken   = 10 vols.
Oxygen taken   = 5 "

Residual vol. after
  combination, RV = 3 vols.

RV taken   = 2 vols.
Oxygen taken   = 1 vol.

R₂V   = 3 vols.

RV taken   = 1 vol.
Hydrogen taken   = 2 vols.

R₃V   = 2.5 vols.
Hydrogen taken   = 2 "

R₄V   = 4.5 vols.

9. Gas-volume = 100 c.c. at 20°, and 760 mm. pressure. What would this volume become at 50°, and 720 mm.?

10. Calculate the percentage of elementary constituents in the compound whose formula is C_2H_6O.

11. What is the formula of the compound which contains 40.00 per cent of carbon, 6.67 per cent of hydrogen, and 53.33 per cent of oxygen?

CHAPTER IV

RELATION BETWEEN VOLUME, PRESSURE, AND TEMPERATURE OF GASES

[THESE topics belong strictly to the subject of Physics, but inasmuch as all measurement of gas-volume involves the application of these laws, a brief study of them is here presented. If the student has already a knowledge of them from a previous course, this chapter may suitably be passed by.]

1. The Law of Boyle

Relation between Volume and Pressure of Gases

In a confined mass of gas, the temperature remaining con- **66** *stant, the volume is inversely proportional to the pressure ; or, the product of the volume by the pressure is constant.*

COROLLARY.—*Density is directly proportional to pressure* **66/2** *when temperature and volume remain constant, and it is inversely proportional to volume when temperature and pressure remain constant.*

The law was first discovered by Robert Boyle about 1662. **66/3** Among Continental writers especially, it is often designated by the name of Mariotte, who, however, did not publish it until 1679.

2. The Law of Charles

Relation between Volume and Temperature of Gases

The volume of a mass of confined gas, the pressure remain- **67** *ing constant, increases by $\frac{1}{273}$ or 0.00367 of itself at $0°$ for each increase of one degree in temperature ; or its pressure increases at the same rate, the volume remaining constant.*

67/1   COROLLARY.—*The laws of Boyle and Charles may be expressed in one as follows : The product of volume by pressure is proportional to the absolute temperature (that is, the observed temperature plus 273 degrees).*

67/2   The law is also designated sometimes by the name of Gay-Lussac, and sometimes by that of Dalton. It was discovered by Charles about 1787.

67/3   NOTE I.—Gaseous substances tend to depart appreciably from these laws as they approach their points of liquefaction.

67/4   NOTE II.—The laws of Boyle and Charles apply to gases in general, independently of the chemical character of the substances.

CHAPTER V *

THE RELATION BETWEEN EQUIVALENT AND COMBINING WEIGHTS AND CERTAIN SPECIFIC PROPERTIES

In studying the qualitative side of chemical phenom- 68 ena, you have been led to see somewhat of the nature of chemical change as involving the disappearance of some kinds of matter, and in their place the appearance of different kinds—what has been called the change of identity in substances. The contemplation of this phenomenon gains in impressiveness with the thought that by mastering thus the production of new substances man perhaps approaches as near to independent creation as is permitted to him in any form of his material activities. Certain it is that he has made in the laboratory not only many substances which are identical with the natural products, but innumerable others as well, which have never been found in nature.

But in further studying these phenomena, particularly 69 their quantitative aspect, you learn, in addition, the perfectly definite conditions imposed on such changes, and hence the limitation imposed on man's productiveness. Thus, no new substances can be made, save from those which contain the same elementary constituents; that is, the constituent elements must be common· to both factors and

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* If the instructor prefers to introduce at this point a part or the whole of Chapter VIII before taking up Chapters V, VI, and VII, no embarrassment will be found in so doing. The writer prefers the order herein followed.

products, and the change is simply a change in their distribution. Nor can any kind of matter be produced without the disappearance of an equal mass of some other kind or kinds.

70   Summing up the laws of quantity in the definition of the equivalent and the combining weights, and accepting these for the present as determined values, we pass on to study the numerical relation between these values and others which measure very diverse properties. The first of these to be considered is the specific gravity of substances in the gaseous condition.

1. The Law of Gay-Lussac

Relation between Equivalent and Combining Weights of Gases, Elementary and Compound, and their Specific Gravities

71   The specific gravity of a gas is defined as the ratio between the weights of equal gas-volumes of the substance and of hydrogen, at the same temperature and pressure. This is sometimes conveniently termed the *vapor-density* to distinguish it from the specific gravity of the substance while in liquid or in solid condition.

It is experimentally easier to weigh air than hydrogen; therefore experimental results are often referred to air as the standard. Such values are converted to the hydrogen standard by the factor 14.40, which is the specific gravity of air referred to hydrogen as unity.

A

In the accompanying Table II, A, No. 93, are given those of the elements which are gaseous or volatile in conditions which permit the determination of their specific gravity as gases; with these are given also their equivalent weights, their chosen combining weights, and their vapor-densities,

as experimentally determined, hydrogen being the standard. Since the vapor-density in some cases varies greatly with the temperature of determination, and in other cases remains practically constant through a great range of temperature, some data as to temperature of determination are given; also the boiling points.

Inspection of these data shows that in the first group of 72 elements the vapor-density is numerically equal or approximately equal to the equivalent weight. Now, fluorine, chlorine, bromine, and iodine, let it be recalled (see Table I, No. 49), combine with hydrogen in the gas-volumetric ratio of 1 : 1; and thallium combines with chlorine in the same gas-volumetric ratio. It follows that if the equivalent weights in these instances be chosen as the combining weights, the formulas of these compounds—for example, HCl, HBr, etc.—may be interpreted as expressing the relative constituent quantities, measured by gas-volume as well as by weight, since the coefficients of the elementary symbols give the ratio of the gas-volumes.

In the second group it is seen that the vapor-density of 73 oxygen approximates very closely to equality with twice the equivalent weight. If in this case the equivalent weight 7.94 were chosen as combining weight, the formula of water would become HO, or some multiple of this, x (HO), in which the coefficients, being equal, do not give the gas-volumetric composition. If, however, the multiple of the equivalent weight by two is chosen as combining weight, the simple relation with vapor-density reappears, and the formula for water becomes H_2O, or some multiple, x (H_2O), in which the ratio of the coefficients, 2 : 1, gives the ratio of the gas-volumes.

Taking thus the vapor-density as a guide in the choice 74 of the multiple of the equivalent weight which shall be used as combining weight, leads clearly in the case of tellurium to the second multiple, although the approximation is not so close as in the case of oxygen. The same

rule consistently applied to selenium and to sulphur would indicate the third and the seventh multiples respectively instead of the second. These two substances, sulphur especially, show a remarkable variation in vapor-density with temperature, and it is to be noted that the lowest values approximate closely to the second multiple. However, the decisive reasons for the choice of this multiple must be looked for in other relations (see No. 87, Part I).

75   In the third group, as to nitrogen, if 4.64 be used as combining weight, the formula of ammonia must be NH, or some multiple, x (NH), which gives no indication of the gas-volumetric composition. But if the multiple by three (viz., 13.93) is chosen, the simple relation to vapor-density appears as with oxygen, and the formula of ammonia is NH_3, the coefficients 1 : 3 giving the ratio of the volumes of nitrogen and hydrogen (see Table I, No. 49). But in

76   the cases of phosphorus and arsenic, the sixth multiple instead of the third is indicated, while for bismuth the vapor-density is nearer the second than the third, and for antimony it is midway between the third and fourth multiples. In all these exceptional cases decisive reasons for choice

77   must be sought in other relations. The same must be said as to the fourth group, in which zinc and cadmium and mercury show vapor-densities approximately equal to the equivalent weights, and sodium and potassium to one half the equivalent weights. As to the recently discovered elements, helium and argon, the data are incomplete.

78   It must be borne in mind that the values for vapor-density are in most cases affected by much greater uncertainty than are the equivalent weights, since their determination, especially at high temperatures, involves great experimental difficulty. They may, nevertheless, serve to indicate the multiple to be chosen, and their indication, in the absence of reasons for different choice, is accepted, we may say for the present, conventionally.

It is evident that to *choose as combining weight for ele-* **79**
ments the multiple by a whole number of the equivalent
weight which approximates most closely to the vapor-density
has the advantages, first, of correlating in a simple man-
ner the two numerical values; and, second, in many in-
stances, of bringing into one formula the expression of
the proportion by gas-volume, if it is known, as well as by
weight of constituents in compounds. These reasons for **80**
choice of multiple receive additional weight from similar
reasons which are revealed in the study of other widely
different properties which will be presented in subsequent
sections of this chapter. There are also very important
considerations, purely theoretic in nature, which lead to
the same choice. These will be presented in connection
with the atomic theory (Chapter VII). It is proper to add
that the reasons of theory have had historically probably
more influence, and still carry in some minds more weight,
than the reasons of convenience just set forth.

B

In Table II, B, No. 94, are presented a few data as to the **81**
vapor-density of gaseous or volatile compounds which, in-
stead of being limited like the elements, are almost innu-
merable. It is seen that, with the multiples which were
indicated in the preceding paragraph as combining weights
for the elements, the vapor-densities of the compounds ap-
proximate equality uniformly with one half their combin-
ing weights; whereas, with the equivalent weights thus
used for the elements, the vapor-densities in the second
group would approximate equality with the combining
weights, and in the first group with one half the combin-
ing weights, and in the third group with one and a half
times the combining weights. Therefore the use of the **82**
multiples chosen for the elements has still an additional
advantage in bringing the vapor-density, at least of these
and similar gaseous compounds, into simpler relation with

5

the combining weights of the same. And this also gives

83 basis for conventionally *choosing as the combining weight of any gaseous or volatile compound, even one whose gas-volumetric composition is unknown, that multiple of its simplest combining weight which approximates most closely to its vapor-density multiplied by two.*

84   Thus in the gas, methane, 1 gram of hydrogen is combined with 2.98 grams, approximately, of carbon; but carbon is practically non-volatile, therefore the gas-volumetric ratio is not known, and the vapor-density, at least, furnishes no reason to choose other value than 2.98 for the combining weight of carbon; but the vapor-density of the compound is 8.00; hence we may choose the multiple by 4 —that is, 16, or, more accurately, 15.9—as the combining weight of methane, and write its formula C_4H_4. Considerations of a different kind (see No. 436, Part I) have led to the choice of 11.9, the fourth multiple, as the combining weight of carbon, making the formula for methane CH_4.

85   Again, the substance, acetylene, contains carbon and hydrogen in the ratio of 11.9 grams to 1 gram; hence its simplest formula would be C_4H (carbon = 2.98), or CH (carbon = 11.9), and its combining weight 12.9. But its vapor-density is 13.2; therefore 25.8 (12.9 × 2) is chosen as its combining weight, and C_2H_2 is its accepted formula.

85/1 Another substance, benzene, likewise contains carbon and hydrogen in the ratio of 11.9 grams to 1 gram, but its vapor-density is 40. Its simplest formula would be CH, identical with the simplest one for acetylene; but choosing, in accordance with this principle, the multiple by 6, gives the combining weight 77.5 and the accepted formula C_6H_6.

86   In the last two examples is seen still another advantage of the principle under consideration, in that it brings about a distinction in formula and combining weight between different substances of the same composition (compare No. 37/7, Part I). (Such substances are called *isomers.*)

Accepting, then, this conventional rule for the choice of 87 multiple as combining weight in the case of compounds (it is more general than the corresponding rule for elements) we may reason backward to certain maximum values for the elements of exceptional vapor-density. Thus, the substance hydrogen sulphide contains hydrogen and sulphur in the ratio of 1 gram of the former to 15.9 of the latter, and its vapor-density is 17.2. This leads to 33.8 grams as the combining mass, of which the constituents must be 2 grams of hydrogen and 31.8 grams of sulphur. Therefore the combining weight of sulphur can not be more than 31.8. Likewise the vapor-densities of the hydrogen compounds of selenium, phosphorus, and arsenic indicate as maximum values for the combining weights of these elements 78.4, 30.8, and 74.44 respectively. And the vapor-densities of the chlorine compounds of antimony and bismuth indicate as maximum values for these elements 119.5 and 206.5.

Effect of temperature.—The simplicity of this relation 88 between vapor-density and combining weight is somewhat disturbed by the fact that, in the case of some compounds, as of some elements, the vapor-density diminishes with increasing temperature. This seems, however, to reach a limit after a certain interval of temperature. This is especially notable in the cases of iodine, sulphur, selenium, phosphorus, and arsenic among the elements (see Table II, A), and nitrogen tetroxide and ferric chloride among the data of Table II, B.

Another class of exceptional compounds contains those 89 which are also exceptions to the law of gas-volumetric proportions (see No. 47/₆, Part I). These are actually decomposed at the temperature of observation.

Upon these facts and others of the same nature is based the generalization often designated by the name of Gay-Lussac, who published it in 1808 (see also Law 5, Chapter II).

The law may be thus formulated :

90/1 CLAUSE I.—*The specific gravity of an element in gaseous condition, referred to hydrogen as unity, approximates numerically the equivalent weight of the element, or a multiple of the same by a small whole number ; and it approximates equality with the combining weight.*

90/2 CLAUSE II.—*The specific gravity of a compound in gaseous condition* (H = 1) *approximates numerical equality with one half its combining weight.*

The degree of approximation as well as some of the exceptions are seen in the data of the tables.

An alternative statement of the law is this :

90/3 *The combining weight in grams of an element occupies, when in gaseous condition, a volume approximately equal to that of 1 gram of hydrogen at the same temperature and pressure ; and the combining weight of a compound, the volume of 2 grams of hydrogen in similar conditions.*

91 NOTE I.—The relation between the combining weights and the specific gravities of elements in the liquid and in the solid condition is not so simple as in the gaseous condition. There is, undoubtedly, a relation, but in the present state of the science it can not be satisfactorily defined. It may only be said that it is probably a *periodic function* of the combining weights. (The explanation of this may be deferred. See Nos. 423, 589, and 590, Part I.)

92 NOTE II.—The law of vapor-densities may be deduced from the facts of gravimetric and gas-volumetric proportions ; for example, thus : Since 2 grams of hydrogen combine with 16 (using approximate values) of oxygen and form 18 of water, and since the gas-volumetric ratios are $2:1:2$ respectively, it follows that 16 grams of oxygen and 9 of water must occupy a volume equal to that of one gram of hydrogen, which is the relation formulated in the law of vapor-densities. Likewise from the facts of gravimetric proportions and of vapor-densities may be deduced the law of gas-volumetric proportions. (How ?)

TABLE II, A.*—*The Law of Gay-Lussac*

No.	Name.	Equivalent weight.	Factor.	Combining weight.	Vapor-density.	Temperature of observation.	Boiling point.
						Degrees.	Degrees.
1	Hydrogen .	1.0	1	1.0	1.0	....	Below—230
8	Fluorine ..	18.91	1	18.91	18.23	....	Below —95
15	Chlorine ..	35.18	1	35.18	35.83	200	—34
	"	"	"	"	23.3	1560	
32	Bromine ..	79.34	1	79.34	82.77	102	59
	"	"	"	"	52.7	1500	
47	Iodine	125.89	1	125.89	127.7	253	184
	"	"	"	"	63.7	1500	
68	Thallium..	202.6	1	202.6	206.2	1730	Red heat.
7	Oxygen ...	7.94	2	15.88	15.90	....	—186
14	Sulphur...	15.915	2	31.83	112.0	468	446
	"	"	"	"	31.8	1100–1719	
31	Selenium..	39.2	2	78.4	111.0	860	665
	"	"	"	"	82.2	1420	
48	Tellurium .	63.25	2	126.5	130.2	1390–1439	1390
6	Nitrogen ..	4.643	3	13.93	13.91	....	—194
13	Phosphorus	10.267	3	30.8	63.96	313	278
	"	"	"	"	45.58	1708	
30	Arsenic....	24.8	3	74.4	154.2	644	
	"	"	"	"	79.5	1700	
46	Antimony .	39.7	3	119.1	141.5	1640	1300
70	Bismuth ..	68.83	3	206.5	146.5	1640	1640
9	Sodium ...	22.88	1	22.88	12.7	?	742
16	Potassium .	38.82	1	38.82	18.8	?	667
27	Zinc.......	32.45	2	64.90	34.15	1400	930
43	Cadmium .	55.7	2	111.4	57.0	1040	770
67	Mercury ..	99.25	2	198.5	101.0	446–1730	358
73	Helium ...	?	...	?	2.0		Below—230
74	Argon	?	...	?	19.8		—187

* Data mostly according to Ramsay, " Inorganic Chemistry."

TABLE II, B.*—*The Law of Gay-Lussac*

NAME.	Formula.	Combining weight.	Vapor-density × 2.
Hydrogen fluoride.......	HF	19.91	19.99
" chloride	HCl	36.18	36.38
" bromide.......	HBr	80.34	78.10
" iodide	HI	126.89	128.0
Thallium chloride.......	TlCl	237.78	237.4
Water	H_2O	17.88	17.98
Hydrogen sulphide......	H_2S	33.83	34.4
" selenide	H_2Se	80.4	80.54
" telluride......	H_2Te	128.5	129.6
Ammonia..............	H_3N	16.93	17.2
Phosphorus hydride.....	H_3P	33.8	33.1
Arsenic hydride.........	H_3As	77.4	77.8
Antimony chloride......	Cl_3Sb	224.7	224.7
Bismuth "	Cl_3Bi	312.0	327.7
Potassium iodide........	KI	164.7	168.9
Zinc chloride	$ZnCl_2$	135.27	132.8
Cadmium bromide	$CdBr_2$	270.2	267.0
Mercurous chloride......	HgCl	270.1	239.6
Mercuric iodide.........	HgI_2	450.28	468.0
Sulphur dioxide	SO_2	63.59	64.9
Carbon monoxide........	CO	27.79	27.96
" dioxide	CO_2	43.67	43.98
Methane	CH_4	15.91	16.0
Acetylene..............	C_2H_2	25.82	26.4
Benzene...............	C_6H_6	77.46	79.78
Nitric oxide	NO	29.81	30.0
Nitrogen peroxide.......	NO_2	45.69	45.8 at 150°
" tetroxide	N_2O_4	91.38	76.0 at 26°
Ferric chloride	$FeCl_3$	161.1	155.5 at 750°–1077°
" "	Fe_2Cl_6	322.2	308 at 440°

* Data mostly according to Muir, " Principles of Chemistry."

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(See Nos. 40, 159.)

2. The Law of Dulong and Petit

*Relation between Equivalent and Combining Weights of
Elementary Solids and their Specific Heats*

In the accompanying Table III, A, No. 105, are given **95** the specific heats of the solid elementary substances, together with their equivalent weights, the factors which convert the latter into combining weights, the combining weights themselves, and the products of specific heats by combining weights. Inspection shows a relation similar to that in the case of vapor-density. In some cases the equivalent weight, in other cases a simple multiple of the equivalent weight, gives numerically with specific heat a product which approximates equality for all the solid elements. The products average about $6.2 \pm$.

It is seen that the approximation to constancy, save in a **96** few instances, is a remarkably close one, although the combining weights range from 7 to 238, and the values for specific heat are affected with considerable uncertainty. As bearing on this, consideration must be given to the fact that specific heat varies with the allotropic condition of the substances, and with the temperature of determination. This is made evident in the data of Table III, B. Diamond, graphite, and **97** charcoal are allotropic forms of the element carbon, and the table shows how markedly the specific heats of the three forms differ, even at the same temperature of determination. It also shows that the specific heat increases with the temperature, but at a much smaller rate for high than for low temperatures.

These peculiarities appear especially in those substances **98** which give exceptional products like glucinum, boron, carbon, and silicon. As the specific heat tends to increase with the temperature, but at a rate notably diminishing as the temperature rises, it may be surmised that at a sufficiently high temperature the approximation to constancy would be fairly satisfactory.

99   Reasons similar to those suggested in considering the vapor-densities may suitably lead in the case of elementary solids to the choice for combining weight of that multiple of the equivalent weight which, when multiplied by the specific heat, gives the product approximating most closely to 6.2.   This brings the combining weight into simple numerical relation with the specific heat.

100   Attention was first called to this relation by Dulong and Petit in 1819, and they urged the choice of combining weights in accordance with the above suggestion.   This involved some changes in the values then in use, and their recommendation was not adopted until considerably later.

The law which is generally designated by their names may be formulated thus :

101   *The specific heat multiplied by the combining weight gives numerically a product which approximates a constant value, viz., 6.2, for all the solid elements.*

Inasmuch as this product is the quantity of heat, measured in calories (see Part II, $50/_1$), necessary to raise by one degree the temperature of the quantity of the substance equal to the combining weight in grams, the law may be given this **Alternative Statement** :

102   *Quantities of the elementary solids equal to their combining weights in grams have approximately equal heat capacity —that is, they take the same quantity of heat, viz., 6.2± calories, to effect a rise of one degree in temperature.*

Note.—This relation does not hold for liquids nor for gases.

103   Corollary.—*If the specific heat of elements in the free state remains unchanged when they have passed into combination, it follows that the specific heat of a compound, multiplied by its combining weight, and divided by the number of elementary combining masses which it contains, should give numerically a value approximating 6.2± ; in other words, the heat capacity of a compound should equal the sum of the heat capacities of its constituents.*

Experiment shows this relation to hold in many solid compounds which are made up of solid elements, and it is designated as the *Law of Kopp and Neumann*. Thus, spe- **104** cific heat multiplied by combining weight gives a product approximately 12 for the sulphides of iron and zinc, and others like them; whereas the heat capacity of the sulphur, 5.7, plus that of the metal, 6.2±, is 11.9±.

TABLE III, A.*—*The Law of Dulong and Petit*   **105**

NAME.	Equivalent weight.	Factor.	Combining weight.	Specific heat.	Sp. H. × comb. wt.
Lithium	6.97	1	6.97	0.9408	6.6
Glucinum	4.5	2	9.0	0.58	5.2
Boron	3.62	3	10.86	0.5 (?)	5.4
Carbon (diamond)	2.9775	4	11.91	0.459	5.5
Sodium	22.88	1	22.88	0.2934	6.7
Magnesium	12.05	2	24.1	0.250	6.0
Aluminium	8.967	3	26.9	0.225	6.1
Silicon (crys.)	7.05	4	28.2	0.203	5.7
Phosphorus (crys.)	10.267	3	30.8	0.202	6.2
Sulphur	15.915	2	31.83	0.178	5.7
Potassium	38.82	1	38.82	0.166	6.5
Calcium	19.9	2	39.7	0.170	6.8
Scandium	14.6	3	43.8	0.153	6.7
Chromium	17.25	3	51.74	0.100 (?)	5.2
Manganese	27.285	2	54.57	0.122	6.7
Iron	27.80	2	55.6	0.114	6.3
Nickel	29.12	2	58.24	0.108	6.3
Cobalt	29.3	2	58.6	0.107	6.3
Copper	31.56	2	63.12	0.095	6.0
Zinc	32.45	2	64.9	0.0956	6.2
Gallium	23.13	3	69.4	0.079 (?)	5.5
Germanium	17.975	4	71.9	0.0758(?)	5.5
Arsenic (crys.)	24.8	3	74.4	0.0822	6.1
Selenium	39.2	2	78.5	0.076	6.0
Bromine (solid)	79.34	1	79.34	0.0843	6.7
Zirconium	22.425	4	89.7	0.0666	6.0
Molybdenum	47.6	2	95.3	0.0722	6.9
Ruthenium	50.45	2	100.9	0.0611	6.2
Rhodium	51.1	2	102.2	0.058	5.9
Palladium	52.8	2	105.6	0.0593	6.2
Silver	107.11	1	107.11	0.057	6.1
Cadmium	55.7	2	111.4	0.0567	6.3
Indium	37.67	3	113.0	0.057	6.4

* Data mostly according to Muir, "Principles of Chemistry."

TABLE III, A.*—*The Law of Dulong and Petit—(Continued)*

NAME.	Equivalent weight.	Factor.	Combining weight.	Specific heat.	Sp. H. × comb. wt.
Tin	29.525	4	118.1	0.056	6.6
Antimony	39.7	3	119.1	0.0508	6.1
Iodine.............	125.89	1	125.89	0.0541	6.8
Tellurium	63.25	2	126.5	0.0474	6.0
Lanthanum	45.8	3	137.45	0.0449	6.1
Cerium	34.75	4	139.0	0.0448	6.2
Tungsten	91.5	2	183.0	0.0334	6.1
Osmium	47.375	4	189.5	0.0311	5.9
Iridium	47.925	4	191.7	0.0326	6.2
Platinum	48.35	4	193.4	0.0324	6.2
Gold	195.7	1	195.7	0.0324	6.3
Mercury (solid)......	99.25	2	198.5	0.0319	6.3
" (liquid)	.....	..	.....	0.033	...
Thallium............	202.6	1	202.6	0.0335	6.8
Lead	102.68	2	205.36	0.0314	6.4
Bismuth............	68.83	3	206.5	0.0308	6.4
Thorium............	57.725	4	230.9	0.0276	6.4
Uranium	59.45	4	237.8	0.028	6.7

TABLE III, B.*—*The Law of Dulong and Petit*

NAME.	Temperature.	Specific heat.	Sp. H. × comb. wt.
Carbon, diamond........	−50°	0.0635	0.076
" "	+10°	0.1128	1.35
" "	85°	0.1765	2.12
" "	250°	0.3026	3.63
" "	606°	0.4408	5.29
" "	985°	0.4589	5.51
Carbon, graphite........	−50°	0.1138	1.37
" "	+10°	0.1604	1.93
" "	61°	0.1990	2.39
" "	201°	0.2966	3.56
" "	250°	0.325	3.88
" "	641°	0.4454	5.35
" "	978°	0.467	5.60
Wood carbon...........	0°–23°	0.1653	1.95
" "	0°–99°	0.1935	2.07
" "	0°–223°	0.2385	2.84

* Data mostly according to Muir, " Principles of Chemistry."

3. The Law of Mitscherlich

*Relation between Composition, and hence Combining Weight,
and Specific—i. e., Crystalline Form*

The law for present purposes may be thus stated :

Substances which are similar in composition sometimes **107**
show the same crystalline form.

The similarity of composition here referred to is seen in
the following substances :

$$\begin{array}{ll}
\text{Calcium carbonate,} & CaCO_3 \\
\text{Magnesium carbonate,} & MgCO_3 \\
\text{Ferrous carbonate,} & FeCO_3 \\
\text{Zinc carbonate,} & ZnCO_3
\end{array}$$

They all come under the type expressed by the general
formula MCO_3, in which M represents one combining mass
of the metal, and they also show the same form of crystal.
The substance, sodium carbonate, Na_2CO_3, on the other
hand, does not have a composition similar to these, it comes
under a different type; nor does it have the same crystal-
line form.

The significance of this relation in its bearing on com- **108**
bining weight is only of minor importance. Its application
may be thus illustrated : Suppose it has been determined
that the equivalent weight of zinc is 32.5, but that there is
question whether to choose this or its multiple by 2 as the
combining weight. With the former value, the formula for
its carbonate would be Zn_2CO_3; with the latter, $ZnCO_3$.
Suppose now that it is observed to crystallize in the same
form as the carbonates of calcium, magnesium, and iron,
which have the accepted symbols above given; but this
crystalline form is not like that of sodium carbonate, which
substance has the symbol Na_2CO_3. These facts would favor
the choice of 65, rather than 32.5, as the combining weight
for zinc.

The law was discovered by Mitscherlich and announced in 1819.

4. The Law of Raoult (I)

Relation between Combining Weights of Solutes and Specific Depressions of the Freezing Points in Specified Solvent

(See Part I, No. 21)

109   **Preliminary statement.**—It has already been observed and noted (see Part I, 23/$_1$) that the presence of substances in solution tends to lower the freezing point of the solution as compared with that of the pure solvent.

110   **Law of proportionality.**—For the same substance in the same quantity of the same solvent, the depression of the freezing point is proportional to the quantity of the substance dissolved.

110/a   **The specific depression** of the freezing point of a substance in a specified solvent is the depression produced by 1 gram of the substance dissolved in 100 grams of the solvent.

111   **The law** (1882).—Clause I.—*The specific depression of the freezing point multiplied by the combining weight of the solute, when the latter is compound, gives a product* (D) *which is approximately the same for all compound solutes in the same solvent, but differs with different solvents.*

112   Clause II.—*When the solute is elementary, its specific depression multiplied by its combining weight, or a multiple of the latter by a small whole number, gives a product* (D) *which is approximately the same for all elementary solutes and equal to that for compounds in the same solvent, but which differs with different solvents.*

113   **As to data.**—The law finds verification in many instances, but it fails in many others ; and the phenomenon is greatly complicated by the fact that the law of proportionality does not always hold good. This throws doubt on the calculation of the specific depression and of the constant of de-

pression, D. Proportionality often holds while solutions are very dilute, but ceases when they become concentrated. A similar difficulty was noted in connection with vapor-density (see Nos. 88 and 89, Part I) and specific heat (see Nos. 97 and 98), the values for which vary with the temperature of determination.

A very slight illustration of this is seen in the data for **114** sulphur and for iodine as solutes, which are given in Table IV, C (No. 122). The specific depression of the former varies from 0.265° to 0.248° when the concentration varies from 2.4 to 7.2 per cent, while that of iodine varies from 0.272° to 0.251° with a variation in per cent from 2.2 to 3.7.

A great many data for compounds in various solvents **115** have been accumulated. To give some idea of the approach to constancy under the law, a few experimental values are cited in Table IV, A and B (Nos. 120 and 121). An explanation has been offered for such abnormally high products as are found for the last five substances in water solution (No. 121); it is based on the assumption that there is actual decomposition of these substances in solution (compare with Nos. 47/6, 88, and 89).

The observations for elementary substances are few, **116** since but few of the elements are soluble in ordinary solvents without chemical change. In Table IV, C (No. 122) are given the data for the constant of depression (D) in the cases of phosphorus, sulphur, bromine, and iodine. The large factors for phosphorus and sulphur should be noted in comparison with those relative to vapor-density (see Nos. 74 and 76).

The constant of depression, D, for a specified solvent may **117** be determined by averaging the products for a large number of substances of known combining weight, such as are exhibited in Table IV, A and B, for acetic acid and water as solvents; but it may also be obtained by a calculation based upon the freezing point of the pure solvent and the

latent heat of fusion, measured in calories, for 100 grams of the solvent. The calculated and the observed values agree closely in many instances. A few examples are given in Table IV, D (No. 123).

118   **An alternative statement** of Raoult's law may be made as follows: *Masses of solutes which are proportional to their combining weights, or in the case of elements to simple multiples thereof, when dissolved in 100 grams of the same solvent, produce approximately equal effects in depressing the freezing point of the solutions as compared with that of the solvent.*

119   **Method of applying.** — Suppose it is questioned what multiple of 16.9 shall be used as the combining weight of hydrosulphuric acid. Experiment gives 1.05° as the specific depression for this substance in acetic acid. Hence, by Raoult's law,

$$\text{Comb. wt.} = \frac{39}{1.05} = 37 \pm;$$

and the multiple of 16.9 by 2 is chosen, since it approximates most closely to $37 \pm$.

120   TABLE IV, A.*—*Raoult's Law* (*I*)

Solvent, acetic acid.   Freezing point $= 16.75°$.   Constant, $D = 39°$.

Solute.	Formula.	Product, D°.
Alcohol	C_2H_6O	36.4
Ether........................	$C_4H_{10}O$	39.4
Chloroform	CCl_3H	38.6
Glycerine	$C_3H_8O_3$	36.2
Naphthalene	$C_{10}H_8$	39.2
Camphor.....................	$C_{10}H_{16}O$	36.4
Water	H_2O	33.0
Carbon disulphide............	CS_2	38.4
Hydrosulphuric acid	H_2S	35.6
Sulphur dioxide	SO_2	38.5
Sulphuric acid................	H_2SO_4	18.6
Hydrochloric acid.............	HCl	17.2
Magnesium acetate............	$Mg(C_2H_3O_2)_2$	18.2

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(See No. 41/₉.)

Table IV, B.*—*Raoult's Law* (*I*) 121

Solvent, water. Freezing point, 0°. D = 19°.

Solute.	Formula.	Product, D°.
Alcohol......................	C_2H_6O	17.3
Glycerine	$C_3H_8O_3$	17.1
Cane sugar..................	$C_{12}H_{22}O_{11}$	18.5
Acetic acid..................	$C_2H_4O_2$	19.0
Magnesium sulphate...........	$MgSO_4$	19.2
Ferrous "	$FeSO_4$	18.4
Zinc "	$ZnSO_4$	18.2
Copper "	$CuSO_4$	18.0
Hydrochloric acid......	HCl	39.1
Ammonium chloride...........	NH_4Cl	34.8
Potassium "	KCl	33.6
" tartrate.............	$K_2C_4H_4O_6$	36.3
Lead nitrate..................	$Pb(NO_3)_2$	37.4

Table IV, C.—*Raoult's Law* (*I*) 122

Solute.	Solvent.	Concentration. Grams in 100 of solvent.	Spec. D.	Multiple of comb. wt.	D° (exp.).	D° (cal.).
Phosphorus †.	Benzene	0.72	0.392°	30.8×4	48.3	51.0
Sulphur †	Naphthalene.	2.42	0.265°	31.8×8	67.4	69.4
"	"	7.20	0.248°			
Bromine ‡....	Acetic acid..	1.71	0.251°	79.3×2	39.8	38.8
Iodine †......	Naphthalene.	2.19	0.272°	125.9×2	68.5	69.4
"	"	3.72	0.251°			

Table IV, D.#—*Raoult's Law* (*I*) 123

Solvent.	D° observed average.	D° calculated.
Water.......................	18.5	18.9
Acetic acid	39.0	38.8
Benzene	49.0	51.0
Naphthalene	71.0	69.4

* According to Ostwald (Muir), " Solutions."

† According to Hertz, Zeitschrift für physikalische Chemie, VI, 358 (1890).

‡ According to Paterno and Nasini, Berichte der deutschen chemischen Gesellschaft, xxi, 2153 (1888).

According to Nernst (Palmer), " Theoretic Chemistry."

5. The Law of Raoult (II)

Relation between Combining Weights of Solutes and Specific Elevations of the Boiling Temperature in Specified Solvent

124   **Preliminary statement.**—The facts presented in the preceding section relative to the freezing point of solutions are closely paralleled by the facts relative to the boiling temperature of the same. Attention has already been given to the fact that the presence in solution of non-volatile substances, or of substances practically non-volatile in the actual conditions tends to raise the temperature of the boiling solution as compared with that of the pure solvent (compare No. 24/4). This temperature is not to be confused with that of the boiling point, which is strictly the temperature of the vapor, not of the liquid. The term "boiling temperature" is herein used to designate the first.

125   Boiling takes place when the pressure of the vapor which is formed in the body of the liquid just exceeds the pressure of the atmosphere plus the resistance which the liquid offers to the formation and movement of bubbles. Now, the presence of non-volatile substances in the liquid reduces the vapor-pressure for a given temperature, and consequently increases the temperature which is necessary to produce a vapor-pressure equal to the opposing pressure of the atmosphere; in other words, it raises the boiling temperature of the liquid, although the temperature of the vapor, after it has escaped from the liquid—i. e., the boiling point—may be unaffected.

126   **The law of proportionality.**—For the same substance in the same quantity of the same solvent the elevation of the boiling temperature is proportional to the quantity of the substance dissolved.

The specific elevation of the boiling temperature of a

substance in a specified solvent is the elevation produced by 1 gram of the substance dissolved in 100 grams of the solvent.

The law (1886).—CLAUSE I.—*The specific elevation of* **127** *the boiling temperature multiplied by the combining weight of the solute, when the latter is compound, gives a product* (E) *which is approximately the same for all compound solutes in the same solvent, but differs with different solvents.*

CLAUSE II.—*When the solute is elementary, its specific* **128** *elevation multiplied by its combining weight, or a multiple of the latter by a small whole number, gives a product* (E) *which is approximately the same for all elementary solutes and equal to that for compounds in the same solvent, but which differs with different solvents.*

As to data.—The statement made concerning exceptions **129** both to the law of proportionality and to the law of Raoult relative to freezing point is equally applicable to the phenomenon of boiling temperature. There are many verifications, but also many exceptions. Variation from proportionality is seen in the data for sulphur, Table V, F. For a concentration of 1.5 per cent the multiple of the combining weight by 8 gives a good approximation to the expected product; whereas at a concentration of 10 per cent the factor 9 gives the closest approximation. A few of the very many experimental determinations for compounds are given in Table V, E, and those of the available elements in Table V, F.

The constant of elevation, E, for a specified solvent may **130** also be calculated from the experimentally determined boiling temperature of the solvent and the latent heat of vaporization, measured in calories, for 100 grams of the same.

An alternative statement of this law may be made in **131** terms exactly similar to those employed in the law relative to the freezing point of solutions.

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TABLE V, E.*—*Raoult's Law* (*II*)

132 Solvent, alcohol. Boiling point=78.3°. Constant, E=11.5°(calculated).

SOLUTE.	Formula.	Comb. wt.	Product E.	Concentration.	Spec. E.
Naphthalene	$C_{10}H_8$	128	10.0		
Urea	CN_2H_4O	60	11.1		
Benzoic acid	$C_7H_6O_2$	122	12.2		
Mercuric chloride...	$HgCl_2$	271	11.7		
Lithium " ...	LiCl	42.5	13.2		
Potassium acetate...	$KC_2H_3O_2$	98	12.0		

133 Solvent, water. Boiling point, 100°. Constant, E = 5.2° (calculated).

Cane sugar........	$C_{12}H_{22}O_{11}$	342	4.9		
Mannite	$C_6H_{14}O_6$	182	5.0		
Urea	CN_2H_4O	60	4.3		
Boric acid....	H_3BO_3	62	4.8		
Mercuric chloride...	$HgCl_2$	271	5.0		
Cadmium iodide....	CdI_2	366	5.2		
Sodium acetate.....	$NaC_2H_3O_2$	82	9.6		

134 Solvent, carb. disulphide. Boiling point, 46.2°. Constant, E = 23.7° (calc.).

Anthracene	$C_{14}H_{10}$	178	24.4	0.59	0.137°
"	"	"	23.7	4.02	0.132°
Naphthalene	$C_{10}H_8$	128	23.2	2.99	0.181°
"	"	"	21.9	7.54	0.171°
Camphor..........	$C_{10}H_{16}O$	152	21.4	2.02	0.141°
"	"	"	21.1	8.09	0.139°

TABLE V, F.†—*Raoult's Law* (*II*)

135 Solvent, carbon disulphide. Boiling point, 46.2°. Constant, E = 23.7°.

SOLUTE.	Concentration. Per cent.	Spec. E.	Multiple of comb. wt.	Product, E.
Phosphorus	1.58	0.185°	30.8 × 4	22.8°
"	10.80	0.159°	"	19.6°
Sulphur	1.52	0.094°	31.8 × 8	24.0°
"	10.00	0.083°	"	21.0°
Iodine.........	1.27	0.095°	125.9 × 2	23.9°
"	9.00	0.087°	"	21.9°

* According to Beckmann, Zeitschrift für physikalische Chemie, vi, 437 (1890).   † Ibid., v, 76 (1890).

SUMMARY

In summing up the facts presented in this chapter rela- **136**
tive to the elements, it is seen that masses of these sub-
stances, which are proportional to their equivalent weights
or to products thereof by a small whole number, produce
equal, or approximately equal, effects in occupying volume
when in the gaseous condition; in absorbing heat with
equal changes of temperature when in the solid condition;
and in depressing the freezing point and raising the boiling
temperature when in dilute solution by equal quantities of
the same solvent.

Moreover, it is learned that simplicity of relation is **137**
brought about by choosing for combining weight the exact
multiple of the equivalent weight which in the gaseous
state occupies a volume most closely approximating that
occupied by 1 gram of hydrogen in similar conditions of
temperature and pressure, and which in the solid state
requires a quantity of heat most closely approximating
$6.2 \pm$ calories to effect a rise of one degree in tempera-
ture; and that the choice is conventionally made in ac-
cordance with these principles, unless reason is found for
choosing otherwise.

Relative to compounds, it is learned that masses of these **138**
equal to their *simplest* combining weights in grams do
in many instances occupy in gaseous condition approxi-
mately equal volumes, and that this volume is equal to that
occupied by 2 grams of hydrogen at the same tempera-
ture and pressure. And again, for simplicity of relation,
that exact multiple of the simplest possible combining
weight is conventionally chosen for the actual combining
weight which in the form of gas occupies a volume most
closely approximating that of 2 grams of hydrogen. In
addition, it is learned that masses of compounds which are
proportional to their combining weights likewise in many
instances produce equal effects in depressing the freezing

point and in elevating the boiling temperature when in solution under similar conditions.

139   And, finally, in comparing elements with compounds it is to be particularly noted that the combining masses of the elements must generally be multiplied by a small factor in order to produce equal effects with those of the combining masses of the compounds, in respect to the specific properties herein studied.   In the matter of vapor-density (see Table II, Nos. 93 and 94) the factor is generally 2. Exceptions may be noted as follows : for iodine the factor is 2 at low temperature and 1 at high, but it is 2 in relation to freezing point and boiling temperature; for sulphur the factor is 7 at low temperature, 2 at high, and 8 or more in relation to freezing point and boiling temperature ; for phosphorus it is 4 at low temperature and the same for the phenomena of the freezing point and boiling temperature ; for arsenic, relative to vapor-density, it is 4 at low and 2 at high temperature, while it is 1 for sodium, potassium, zinc, cadmium, and mercury.

140   Relative to specific heat, on the other hand, the factor varies and is equal to the number of elementary combining masses which the compound contains.

141   Great significance is attached to the facts of this chapter, and important theoretic conceptions are based upon them.   The correlation of these widely diverse phenomena, and there are likewise others which have not been here presented, with those of chemical change can not but be impressive to the thoughtful student of nature.   It forces upon him the conviction that there must be some cause underlying the common relation ; and men have not been slow in their attempts to discover and explain this cause. The outcome of their efforts will be set forth in connection with the atomic theory in Chapter VII ; but, preceding this, it is well to give brief consideration to the method of determining experimentally these fundamental values, the equivalent and combining weights.

CHAPTER VI

METHOD OF DETERMINING EQUIVALENT AND COMBINING WEIGHTS OF ELEMENTS AND FORMULAS OF COMPOUNDS

1. Determination of the Equivalent Weight of an Element

THE equivalent weight of an element has already been **142** defined (see Nos. 42 and 43). The most direct method of determining its value is to ascertain by experiment what mass of the substance combines with 1 gram of hydrogen. If it combines in more than one ratio with hydrogen, under the law of multiples, more than one value will be found. For convenience the smallest might be designated, although this is not important. If it forms no compound with hydrogen, it is necessary to determine its ratio of combination with some element, the equivalent weight of which has been determined. Many of the elements do not combine with hydrogen, or, if they do so combine, they form compounds not so well suited for analysis as those with some other element. On the other hand, most of the elements do combine with oxygen and furnish compounds **143** available for analysis. With chlorine, also, many advantageous compounds are formed. And so, historically, the oxides and chlorides have been more frequently used than the hydrides, and in some instances other and more complicated compounds than these have served.

To determine the equivalent weight, therefore, it is ne- **144** *cessary to ascertain by experiment what mass of the element combines with 1 gram of hydrogen, or, if this is impracticable, with 7.94 grams of oxygen, or 35.189 grams of chlorine, or with the equivalent mass of some other substance.*

145   There is no need to consider here the details of experimental procedure. The most refined analytical methods known and available to chemists have been brought to bear upon the determination of these fundamental values. Not by any means the same degree of accuracy has been attained in all instances.   The values given for the combining weights in Table XI, No. 644, have in most instances an uncertainty of one or two units in the last figure.   The greatest accuracy is claimed for that of silver, with an uncertainty of less than four units in more than one hundred thousand, an accuracy " which has scarcely been obtained elsewhere in the exact sciences, much less surpassed." *
The name of Stas (1860–1865), a Belgian chemist, is memorably associated with this great work.

146   Several other values show an uncertainty of only a few units in ten thousand or more, while in others it is as much as one per cent.   The combining ratios of oxygen and chlorine with hydrogen are especially important, being the values upon which many of the others depend, and vast labor and great skill have been brought to bear upon their determination.   In spite of this, the equivalent of oxygen, until a comparatively recent date, has been affected by an uncertainty as great as one part in two hundred.   For this reason it has been proposed to fix this value as eight— that is. to make 8 grams of oxygen the base of the system instead of 1 gram of hydrogen, letting the uncertainty lie upon the value for hydrogen, the equivalent weight of which would become one and a small fraction.   The combining weights reckoned on this basis ($O = 16$) are also given in Table XI, No. 644.

147   By experiments involving the greatest skill and most elaborate apparatus, Morley, of Cleveland (1895), and others, have determined the mass of oxygen which combines with 2 grams of hydrogen as 15.879, with a probable error of

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* Ostwald (Walker). " Outlines of General Chemistry."

only a few units in about sixteen thousand.   A few of Morley's results are here quoted as of interest :

15.877
15.877
15.877
15.878
15.879
15.881
15.881
15.882

15.8792 = the mean of these and others.

As of special interest, also, in connection with your ex- **148** periment under Law 4, Chapter II (No. 41/2), are quoted some recent results in determining with the utmost exactness the mass of zinc which combines with 16 grams of oxygen, by converting a weighed quantity into nitrate, igniting, and weighing the oxide obtained :

65.459
65.445
65.459
65.440
65.489
65.475
65.437
65.447

65.457 *

In the case of some of the metals, the experimental de- **149** termination of the ratio of hydrogen displacement, as illustrated in your experiments (Nos. 41/3 and 41/4), is useful, but rather as a secondary method of control than as a direct determination of the equivalent weight.

* Morse and Arbuckle, American Chemical Journal, xx, 195 (1898).

2. Determination of the Combining Weight of an Element

150   The choice of that multiple of the equivalent weight which shall be designated as the combining weight is controlled by such one or several of the relations given in Chapter V as may be applicable to the element in question. In the event of conflicting indications, the law of Gay-Lussac probably carries the greatest weight, and next to this the law of Dulong and Petit.   The laws of Raoult have come into use in only comparatively recent years, and have given valuable indications in many cases in which the data for the application of the other laws were lacking.

151   Besides the reasons for the choice of multiples, which are found in the correlation of the specific properties studied in Chapter V, a very important aid is obtained in considering the relation of the element to other elements through its general properties.   This relation is embodied in the law of periodicity (see Chapter VIII, Nos. 436 and 589, Part I), the presentation of which is best deferred until after a somewhat detailed descriptive study of the elements themselves.   Suffice it for the present to state, by way of illustration, that the relation of carbon to the other elements, now expressed by the law of periodicity as dependent on the combining weight 12, would be quite inexpressible as dependent on any other multiple of its equivalent weight 3, if the other elements retained their present values.

152   It may be well to emphasize by repetition here what is implied in all the foregoing study, that these relations with specific properties are used only to determine the choice of that exact multiple by a whole number of the equivalent weight which shall be used as combining weight, and not to determine the fundamental ratio itself, which is expressed in the equivalent weight.   This value is determined by chemical analysis with a precision which, save in a few in-

JOSEPH LOUIS GAY-LUSSAC

B. France, 1778. D. Paris, 1850.

(See Nos. 47/7, 89, 220.)

stances, far exceeds that reached in the measurement of the specific properties. The approximations in the latter are, however, usually sufficient to distinguish clearly between different multiples.

3. Determination of the Formula of a Compound

The first step in the solution of this problem must be to **153** determine qualitatively what elementary constituents the given compound contains. It suffices, and may be more convenient, to learn the proximate constituents, if the composition of the latter is known. Thus carbon dioxide may be recognized as a constituent of sodium carbonate (compare Exps. Nos. 35 and $81/_1$), and by this it is known that carbon and oxygen are among its elementary constituents. It is often more practicable to convert an elementary constituent into some recognizable compound, than to separate and identify it in its elementary condition. Thus, if a compound is combustible, and water is identified as a product of its combustion, the presence of hydrogen as a constituent is proved (compare Exps. $34/_2$ and $34/_4$).

The second step must be to ascertain, as accurately as **154** possible, the quantities of the elements present in a measured quantity of the compound. And here likewise, it may be necessary to convert the elements quantitatively into forms of known composition, suitable for measurement. The results of such quantitative determination are usually expressed as parts found in one hundred parts of the compound taken.

To deduce a formula when the percentage composition **155** is known, divide the percentage of each constituent by the combining weight of the same. A series of quotients is thus obtained which should stand to each other in a ratio closely approximating that of whole numbers; if the whole numbers desired do not appear on inspection, divide the quotients by the smallest of the series. Write the symbols of

the elementary constituents together to form the symbol of the compound, and attach to them, as coefficients (written below the line), the simplest set of whole numbers which stand in the ratio of the quotients. This formula shows the percentage composition of the substance, and the sum of the constituent weights becomes its combining weight, unless there be found some reason for choosing a multiple of this formula and this combining weight, as indicated by the law of Gay-Lussac, or those of Raoult. Of these the former is reckoned as giving the surer indication. There are many compounds, however, to which neither can be applied.

155/1   The following example of actual experimental results is taken from a recent journal : *

	Experiment I.	Experiment II.
Carbon............	12.00 per cent	11.69 per cent
Hydrogen.........	3.98 "	4.02 "
Nitrogen..........	6.77 "	
Bromine..........	77.56 "	
	100.31 "	

$$12.00 \div 11.9 = 1.008$$
$$3.98 \div 1.0 = 3.98$$
$$6.77 \div 13.9 = 0.487$$
$$77.56 \div 79.3 = 0.978$$

$$1.008 \div 0.487 = 2.07$$
$$3.98 \div 0.487 = 8.17$$
$$0.487 \div 0.487 = 1.0$$
$$1.978 \div 0.487 = 2.01$$

Hence is deduced the formula $C_2H_8N_1Br_2$, which expresses the following percentages to which the experimental values approximate :

$$\text{Carbon} = 11.65$$
$$\text{Hydrogen} = 3.92$$
$$\text{Nitrogen} = 6.80$$
$$\text{Bromine} = 77.63$$
$$100.00$$

156   EXAMPLES.—(1) Deduce the formula of the compound from the following data : 92.30 per cent of carbon, 7.70 per cent of hydrogen; specific gravity as a gas (H = 1) is approximately 38.

(2) Also for 40.00 per cent of carbon, 6.67 per cent of hydrogen, and 53.33 per cent of oxygen; specific gravity, as a gas, is approximately 29.

(3) Also for 78.86 per cent carbon, 10.60 per cent hydrogen, 10.53 per cent oxygen.

(4) Assume that 1 gram of a substance (e. g., alcohol) containing only carbon, hydrogen, and oxygen yields by burning 1.913 grams of carbon dioxide and 1.173 grams of water (the quantity of oxygen is assumed to be the difference between the total and the sum of the carbon and the hydrogen); assume that the specific gravity of the gas is approximately 23; deduce the percentage of carbon, hydrogen, and oxygen, and the formula of the substance.

(5) Experiment gives for ferric chloride the vapor-density 10.7 (air = 1) and the percentage of chlorine 65.76; also the specific heat of iron as 0.114; assume for the combining weight of chlorine 35.2 and deduce the combining weight of iron and the formula of iron chloride (Meyer and Grünwald).

(6) What percentage of chlorine is contained in ammonium chloride?

(7) What is the percentage of iodine in mercurous iodide? In mercuric iodide?

(8) Assume that 10 grams of pure iron displace 0.36 of a gram of hydrogen from hydrochloric acid; calculate the equivalent weight of iron.

(9) What weight of oxygen should be obtained by heating 10 grams of pure potassium chlorate?

(10) What is the percentage of carbon dioxide contained in calcium carbonate?

THE ATOMIC THEORY

157   It is the purpose of this chapter to present under this general title the prevailing theories which have been devised to explain the facts already set forth, as well as many other facts impracticable of treatment in an elementary study.

158   Some writers on the history of chemistry endeavor to trace the origin of the atomic theory back to Greek and Latin speculative writers, who did indeed discuss the nature of matter, its infinite divisibility, and kindred subjects; but this was rather metaphysical speculation, and may hardly be regarded as related to physical science in the strict meaning of the term.

159   To Dalton, a chemist and physicist of Manchester, England, is credited the invention of the atomic theory, since he was the first to give it quantitative form, and to make it a truly scientific hypothesis, to be tested by experiment and observation.   This he did between 1803 and 1806, and he was led to the conception largely by his discovery of the fact of multiple proportions.   Since then the theory has been greatly modified by change and extension, but still preserves his fundamental idea.

160   In order to present the theory as a whole, and logically

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* If the instructor desires to defer the presentation of the Atomic Theory until later in the course, there is nothing in the arrangement of the subject-matter to hinder so doing.

rather than chronologically, it is necessary to give attention, first, to a purely physical hypothesis as to the constitution of matter. The assumption which most satisfactorily explains many facts in the domain of physics is that gross matter—that is, matter as it appears to the senses—is an aggregation of very small material particles, separated by intervening spaces, and that these particles are the units (or individuals, so to speak) upon which act different kinds of energy, such as heat, light, and electricity. The supposition is that substances (for example, glass), although they appear homogeneous, are in reality grained, and would so appear to a sufficiently magnified sense—as a pile of shot, at a distance, would seem homogeneous, but, seen closely, would show its grained structure.

These particles are called *molecules*, and the theory is **161** named the *molecular theory*. Upon it depends largely the explanation of the important phenomena of light and of heat, such as expansion and contraction with change of temperature, the solid, liquid, and gaseous states, and, in respect to the latter, the law of Boyle and that of Charles.

These molecules are reckoned as real magnitudes, fur- **162** nishing as definite a basis for mathematical reasoning as if they could be individually weighed on the balance. They are much smaller than anything revealed by the most powerful microscope, yet they are capable of approximate measurement by indirect calculation. Lord Kelvin, the eminent English physicist, has estimated that if a drop of water were magnified to the size of the earth, and its molecules in the same proportion, the mass would appear more coarsely grained than a heap of small shot, but less coarsely grained than a heap of baseballs. Or again, a cube one four-thousandth of a millimeter or one one-hundred-thousandth of an inch on the edge is about the smallest mass to be seen by a good microscope, and this contains from sixty millions to one hundred millions of molecules. Such magnitudes are

so far beyond the range of ordinary experience that they seem as inconceivably small as the celestial dimensions seem inconceivably large.

The atomic theory (or the atomic-molecular theory, as it might be called) in its present form involves the following fundamental assumptions:

163   1. **The molecular constitution of matter.**—It is assumed that gross matter is an aggregation of very minute material particles, separated by intervening spaces. These particles, called molecules, act as units to all forces other than chemical.

164   2. **The kinetic theory of gases** (due largely to Clausius, 1857) assumes that in the gaseous condition the separating spaces are considerable as compared with the size of the molecules; that the molecules are in rapid motion in all directions, colliding constantly with each other and with the walls of the containing vessel, and, being perfectly elastic, rebounding after every collision; and that gas pressure is due to this impact on the walls. From these assumptions, and by the application of the laws of mechanics, may be deduced the laws of Boyle and Charles, which also have a purely experimental basis, as has been already described.

165   3. **Avogadro's hypothesis.**—It is assumed that equal volumes of all gases, independently of their chemical character, at the same temperature and pressure, contain the same number of molecules. This was put forth as a hypothesis by Avogadro in 1811, but it may also be deduced from the kinetic theory of gases which was developed considerably later.

166   4. **The chemical definition of a molecule** defines it as the smallest mass of a substance in which the properties of the substance inhere; that is, the identity of a substance is conceived as resident in its molecule. It is assumed that all molecules of the same substance are alike and have the same mass.

5. **As to molecular weights.**—It is assumed that the rela- **167** tive mass of molecules of different substances, referred to the molecule of hydrogen as unity, is equal to the specific gravity of the substance in gaseous condition, referred to hydrogen as standard. It follows that the values which have been called the combining weights of compounds are by this theory called their *molecular weights* (in this sense not expressible in grams), and that the molecular weight of hydrogen, and of some other elementary gases, is twice the combining weight. This assumption is a direct deduction from the laws of Gay-Lussac (see Part I, Nos. 47, 90/$_1$, and 90/$_2$) and the hypothesis of Avogadro.

6. **The divisibility of the molecule of a compound** into **168** smaller parts which are unlike each other, and unlike the original molecule, is assumed because a measured mass of the compound can be separated into smaller masses of its elementary constituents. Thus, since 18 grams of water can be separated into 2 grams of hydrogen and 16 grams of oxygen, it is assumed that the molecule of water, weighing nine times as much as the molecule of hydrogen, can be, and in the decomposition of water is, separated into smaller parts of two different kinds, called atoms, one in the aggregate showing the properties of hydrogen, and the other those of oxygen. Compare No. 172.

7. **The divisibility of the molecule of an element,** at least **169** of some elements, is assumed, and the assumption is based on reasoning, of which the following is an example : It is a fact that one gas-volume of hydrogen and one gas-volume of chlorine combine and form two gas-volumes of hydrochloric acid (see Part I, No. 49/$_1$). It is assumed that two gas-volumes of the compound contain twice as many molecules as one gas-volume of hydrogen and twice as many as one gas-volume of chlorine. It is also assumed that every molecule of hydrochloric acid contains its smaller particle of hydrogen and of chlorine. Therefore it is assumed that every molecule of hydrogen, likewise of chlorine, is divisible

into at least two equal and like parts, since the hydrogen molecules are distributed among twice their number of molecules of hydrochloric acid. Exactly similar reasoning leads to the assumption that the molecules of oxygen in forming water, and those of nitrogen in forming ammonia, are divided into at least two equal and like parts. And the same is true of most of the elementary gases. These smaller particles are named *atoms*.

170   This assumption in distinguishing between the molecule and the atom of elements interprets the facts concerning vapor-density (see Nos. 72, etc., 93, and 94) as indicating that the molecule of hydrogen and that of most of the elementary gases contain two atoms; that the molecule of iodine contains two atoms at low temperature, but only one at high—in other words, the atom and molecule become the same; likewise the molecule of sulphur contains seven or eight atoms at low and two at high temperature; that of phosphorus and that of arsenic contain four atoms; while the molecules of sodium, potassium, zinc, cadmium, and mercury contain but one atom. See Nos. 139 and 141.

171   8. **The atom is defined** as the smallest mass of each elementary substance that is found in any molecule; it is the unit upon which chemical force acts, remaining undivided through all changes. It is assumed that all atoms of the same element are alike, but unlike the atoms of every other element.

172   It is customary to speak of the atoms of hydrogen and of the atoms of oxygen, yet we may not be justified in assuming that an aggregation of such atoms, uncombined in molecules, would show the properties of hydrogen and of oxygen.

173   9. **As to atomic weights.**—It is assumed that all chemical changes are due to the interaction of atoms; and that the relative mass of atoms of different elements, referred to the atom of hydrogen as unity, is constant and numerically equal to the combining weight of the element. Therefore

the values which have been called combining weights of the elements are by this theory called the *atomic weights* (in this sense not expressible in grams). It follows that the formula of a compound shows the kind and number of atoms in its molecule.

This assumption constituted the atomic theory as first **174** announced by Dalton in 1804. It is simply a theoretic interpretation, or explanation, of the facts embodied in the laws of fixed, multiple, and equivalent proportions.

10. **As to heat capacity.**—It is assumed that all atoms **175** have the same heat capacity (see Nos. 101 and 102). This is but the theoretic interpretation of the law of Dulong and Petit.

11. **As to Raoult's laws.**—The theoretic statement is that **176** the effect of a solute in lowering the freezing point and in raising the boiling temperature of a solvent is dependent on the number and not on the kind of molecules of the solute present in a specified mass of the solvent. The observations concerning sulphur and phosphorus and iodine in solution are interpreted as indicating eight, four, and two atoms respectively in the molecule (compare Nos. 116, 122, 135, 139, and 141). The exceptional values for compounds, such as those seen in the last three items of the table, No. 120, are thought by some to indicate, for the substances when dissolved in the specified solvent, a molecular weight which is double the formula weight given in the table. On the other hand, values such as those seen in the last five items of No. 121 and in the last item of No. 133 are interpreted as indicating, not that the molecular weights of the substances in question are one half those assigned in the table, but that the substances are actually decomposed in the conditions of observation into elementary or into proximate constituents, so that there are twice as many molecules present as there would be without decomposition. This assumption as to the peculiar condition of some substances when dissolved in some solvents is the basis of

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what is known as the theory of *electrolytic dissociation* or of *ionization*. It was advanced by Arrhenius in 1887, and it includes the theoretic interpretation of many of the phenomena of solution besides those pertaining to the freezing point and to the boiling temperature.

177   12. **As to the structure of molecules.**—It is assumed that the properties of substances are affected not only by the kind and number of atoms in the molecule, but also by their arrangement, grouping, or linkage.

178   The discovery in 1828 by Wöhler that two different substances may have the same percentage composition found no explanation in the theory of that time, which assumed that the properties of the compound were dependent only on the kind and number of its constituent atoms. Since then very many instances have been revealed of substances which are identical in percentage composition, but still very different in properties (compare Nos. $37/_7$, 85, $85/_1$, and 86). This has led to the assumption of molecular structure to explain the existence of such substances, and many of the most conspicuous achievements of modern chemistry may be properly regarded as the outcome of this conception, or of experiments guided by it.

179   Substances having the same percentage composition, but not identical, are called *isomers*. Of these there are two varieties—the *polymers* and the *metamers*. The *polymers* are substances which have the same percentage composition, but differ in molecular weight. For example: the two substances acetylene, C_2H_2, and benzene, C_6H_6, are polymers. In terms of the theory, the molecule of the first contains two atoms of carbon and two of hydrogen, while that of the second contains six atoms of carbon and six of hydrogen.

180   The *metamers* are substances which have the same percentage composition and the same molecular weight. Their difference of properties is theoretically explained as

due to difference in the grouping of the constituent atoms of the molecule. This is expressed in their formulas by a difference in the grouping of the symbols. For example: the first instance of isomerism, discovered by Wöhler, was in the two substances ammonium cyanate, a salt, NH_4CNO, and urea $(NH_2)_2CO$, a very different substance having not even the general characteristics of the salts. The difference in structure is shown in the different arrangement or grouping of the elementary symbols.

Evidence as to structure.—The subject of structure finds **181** its greatest development in the study of the carbon compounds, usually called organic chemistry, and no detailed consideration of it is judged suitable for a course having the scope of this one. It is desired, however, to give a suggestion concerning the kind of evidence upon which assumptions as to structure are based. For illustration, take the substance known as acetic acid. It contains the elements carbon, hydrogen, and oxygen. The percentage of these gives the formula CH_2O, the combining weight of which would be 30. But the specific gravity of the substance in gaseous condition indicates the combining weight 60; therefore the molecular formula of the substance is $C_2H_4O_2$. This is polymeric with another very different substance which has the formula CH_2O. Now, it is observed that the substance $C_2H_4O_2$ acts as an acid—that is, it contains hydrogen which can be replaced by the action of metals, forming a series of well defined salts. But experiment shows also that only one fourth of the hydrogen contained can be thus replaced. The theoretic interpretation of this is, that one of the four hydrogen atoms is held or linked in the molecule in a manner somehow differing from that of the other three, and this, the first step in differentiating the atoms in the structure of the molecule, is expressed by writing the formula $H(C_2H_3O_2)$.

Again, experiment shows that by acting upon acetic **181/1** acid with a certain substance there is obtained from it a

substance which, when compared with the original in composition, shows the loss of one atom of hydrogen and one of oxygen and the gain of one atom of chlorine—that is, one atom of chlorine has been substituted for one of hydrogen and one of oxygen, but no more than these two can be thus substituted. The theoretic interpretation of this is that one atom of hydrogen and one of oxygen are held in a peculiar manner not shared by the other atoms of hydrogen and oxygen. Furthermore, the derived substance, C_2H_3OCl, does not show the property of substituting a metal for the hydrogen; therefore it is assumed that the hydrogen atom, thus associated with the oxygen atom in leaving the molecule, is the same that in the original substance was replaceable by a metal. This, the second step in solving the molecular structure, is expressed by writing the formula $HO(C_2H_3O)$.

181/2   It is next shown by experiment that acetic acid can be made synthetically, by a series of changes not necessary to detail, from a substance whose molecule contains but one carbon atom, three hydrogen atoms, and the group OH. Its structure is shown by the formula CH_3OH. The change of this into acetic acid involves the addition to the molecule, CH_3OH, of a carbon atom from a source outside of itself, and some subsequent intermediate modifications; but it is assumed that the atomic group CH_3 passes, itself unmodified, from the parent molecule, CH_3OH, into the product, $HO(C_2H_3O)$, and continues to exist in the latter. This resolves the atomic group C_2H_3O into the groups CO

181/3   and CH_3. Thus the original molecule containing two carbon, four hydrogen, and two oxygen atoms ($C_2H_4O_2$) has been resolved into atomic groups as expressed by the symbols HO, and CO, and CH_3. This is shown in the structural or constitutional formula $CH_3 \cdot CO \cdot OH$.

182   By observations and assumptions, such as these just described, the structures of hundreds of substances have been determined, many of them very complicated. Not

only is this true, but also that many natural substances, and even many never found in nature, have been made artificially by building them up from simpler substances as indicated by the atomic groups in their assumed structure. It is doubtful if any branch of natural science can show more numerous instances of brilliant achievements in fact, realized under the guidance of theoretic conceptions, than can synthetic chemistry.

13. **As to space relations of atoms, or stereo-isomerism.**—It is **183** assumed that the properties of substances may be influenced to a limited extent by the space relations of the atomic groups.

The discovery made by Pasteur in 1848, that substances **184** might have not only the same percentage composition, the same molecular weight—i. e., the same kind and number of atoms in the molecule—but even the same atomic grouping, and still differ slightly in respect to certain properties, could not be explained by the then existing theories. The substance in which this phenomenon was first observed by Pasteur is *tartaric* acid, found in the grape and other fruits. The properties in which the slight difference is manifested are crystalline form, and behavior toward polarized light. It would be entirely impracticable fully to describe here either the phenomenon or the theory.   Let it suffice to say that Pasteur observed at least two varieties of tartaric acid.   One when in solution rotates to the right the plane in which a ray of light is polarized ; the other rotates it to the left.   The two varieties, when crystallized, show two kinds of crystals, one of which, as to arrangement of angles and faces, is like the image of the other as seen in a mirror. Yet, as to behavior in all their reactions, the two varieties are alike, and therefore, it must be assumed, have the same structure or atomic grouping.   This phenomenon is called *physical isomerism*, or *stereo-isomerism*.   Many other examples of it have since been discovered.

In 1874 Le Bel and van't Hoff, independently of each **185** other, announced a theory designed to account for the

phenomenon of physical isomerism. They both had the same fundamental idea. According to this, the carbon atom, which is capable of uniting with four hydrogen atoms, or four groups of atoms, as seen in methane, CH_4, furnishes one condition for the phenomenon. It is assumed that these four atoms or groups are placed, with reference to the carbon atom, like the four apexes of a tetrahedron with reference to its center. Now, it is evident that, if every one of four such atoms, or groups, is different from every other one, there might be in two molecules, otherwise alike, the same difference in the position of the four with reference to the carbon atom as there is in the four apexes of a tetrahedron with reference to its center, compared with the same as seen in the image of the tetrahedron reflected in a mirror. A carbon atom thus linked with four different atoms, or groups, is called *asymmetric*, and its presence in the molecule is supposed by the theory to be the cause of stereo-isomerism. For example, the accepted structure of the molecule of lactic acid, the acid of sour milk, is shown by the formula

$$\overset{\displaystyle H}{\underset{\displaystyle OH}{CH_3 - C - CO \cdot OH,}}$$
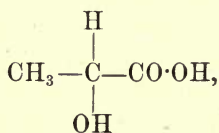
in which it is assumed that one carbon atom is linked with four different groups, viz., CH_3, and H, and OH, and $CO \cdot OH$. It is, therefore, asymmetric, and the substance should show the phenomenon of physical isomerism, as in fact it does. The theory has been admirably worked out, and finds strong support in many recognized facts.

186   Much more is included in this chapter than the atomic theory of Dalton contained, and more than this title accurately describes. But the title is classic, and serves its purpose probably as well as would any other single phrase. That these theories leave much unexplained, is surely true.
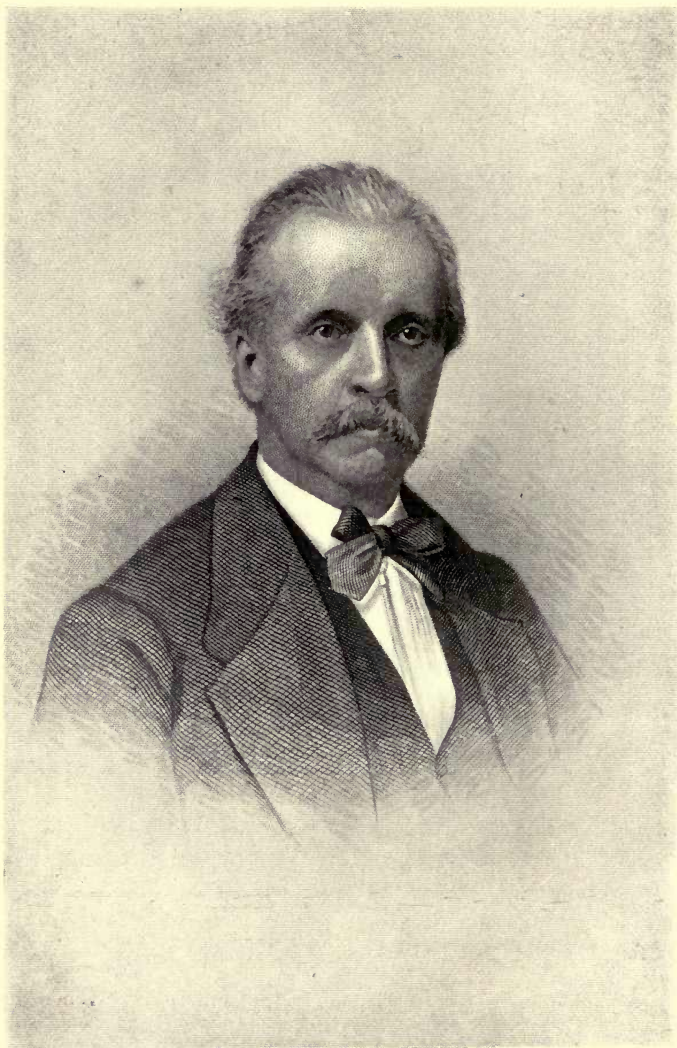
HERMANN VON HELMHOLTZ

B. Germany, 1821.   D. 1894.

(See No. 50, note.)

That they explain with entire satisfaction all that they undertake to explain, is not wisely claimed. That they may not in the future be greatly modified, and even essentially changed, it is not in accordance with the scientific spirit to assert. But that they have been and are useful as guide to investigation and as aid to understanding, is amply proved by the results achieved.

CHAPTER VIII

RELATION BETWEEN THE PROPERTIES OF THE ELEMENTS IN GENERAL AND THEIR COMBINING WEIGHTS

187 IT is the purpose in this chapter to present a somewhat detailed description of the first twenty-five elements, taken in the natural order—that is, the order of their increasing combining weights, and in connection with each one, for convenience of arrangement, to give attention to some of its important compounds. This is the subject-matter often designated as Descriptive Chemistry, and includes more, perhaps, than is implied, strictly speaking, in the title of the chapter; nevertheless, the central idea of the whole will be found in the relation to which the title refers.

A. OF THE ELEMENTS, COLLECTIVELY

188 All substances, so far as known, are made up of comparatively few elementary forms of matter, which resist all attempts to reduce them to simpler forms. These, at present, number seventy-four, with possibly one or two additions.

189 Their *distribution* is by no means uniform. Either free or as constituents, all of them are found in the solid mass of the earth; some thirty, in the sea; five, in the atmosphere, namely, hydrogen, carbon, nitrogen, oxygen, and argon (Roscoe); and, according to the revelations of the spectroscope, at least twenty-two and possibly thirty-eight have been identified in the sun (Ramsay).

In *quantity*, too, they differ greatly, so far as known in **190** this fragment of the universe, the earth. Oxygen is the most abundant of all. It constitutes nearly one quarter (23 per cent) of the atmosphere, nearly nine tenths (88.9 per cent) of all the water of the globe, and nearly one half (Roscoe) of the solid portion of the earth's crust, the other half being made up in the main of only seven other elements. The following is the estimated composition of the greater portion of the earth's crust, not including water (Roscoe):

Oxygen,	44.0 to 48.7 per cent	Calcium,	6.6 to 0.9 per cent
Silicon,	22.8 to 36.2 " "	Magnesium,	2.7 to 0.1 " "
Aluminium,	9.9 to 6.1 " "	Sodium,	2.4 to 2.5 " "
Iron,	9.6 to 2.4 " "	Potassium,	1.7 to 3.1 " "

It is probable that the interior mass of the earth consists largely of sulphides (Ramsay).

Adding to the eight of the foregoing list the following six, namely, hydrogen, carbon, nitrogen, phosphorus, sulphur, and chlorine, we have those which constitute the greater part of matter as known to us. Twenty-three more might be named, which, with those already mentioned, thirty-seven altogether, would include about all with which we come in contact in everyday life. Of the remainder, some are found somewhat commonly, although in small quantities; others are so rare as to be only scientific curiosities; and of still others it may be said that their very existence as elemental forms is open to question.

The five most closely associated with the *living organism*, **191** whether plant or animal, are carbon, oxygen, nitrogen, hydrogen, and sulphur. *Protoplasm*, the fundamental form of living substance, contains these, and in proportion probably somewhat as follows:

Carbon,	51	to 55	per cent
Oxygen,	20	to 24	" "
Nitrogen,	15	to 17	" "
Hydrogen,	6.5 to 7.5		" "
Sulphur,	0.3 to 2		" "

Besides these, phosphorus, potassium, calcium, magnesium, and iron are reckoned as essential to plant life.

All of the foregoing are found in the normal human body, and in addition chlorine, fluorine, silicon, lithium, sodium, and manganese (Martin). If any one more than others could be regarded as the basis of living things, it is carbon, by reason both of its peculiar nature and its predominating quantity.

192 Only comparatively few of the elements are found *free*, or *uncombined*, and abundant in nature, at least on the earth. Such are oxygen, nitrogen, carbon (as coal), and sulphur. Less abundant, yet familiar either as natural or artificial products, are some of the metallic elements, namely, magnesium, aluminium, iron, nickel, cobalt, zinc, copper, tin, lead, mercury, silver, gold, and platinum.

193 Of the whole list of elements the following are generally classed as distinctly *non-metallic :* boron, carbon, silicon, nitrogen, phosphorus, oxygen, sulphur, selenium, fluorine, chlorine, bromine, iodine, and the newly discovered substances helium and argon, fourteen in all. The following are classed sometimes as metallic, sometimes as non-metallic : hydrogen, titanium, zirconium, vanadium, arsenic, antimony, and tellurium. The rest are *metallic.*

194 As to physical properties, they vary through an enormous range. At ordinary temperature, seven are gaseous, namely, hydrogen, nitrogen, oxygen, fluorine, chlorine, helium, and argon. Two are liquid—bromine, and mercury.

195 The others are solid. In *boiling point* they vary from that of hydrogen, $-238°$, to that of carbon, which volatilizes only at the highest temperature of the electric furnace, that is, 3,500° or more.

196 In *density,* the extremes are hydrogen, one cubic centimeter of which weighs 0.0000899 of a gram, and osmium, of which the same volume weighs 22.48 grams ; that is, osmium weighs 250,000 times as much as hydrogen, volume for volume.

In *combining weight* they range from 1 for hydrogen to **197** 238 for uranium.

In *chemical activity,* also, they vary greatly.   Thus fluo- **198** rine is so reactive, attacking so energetically everything with which it comes in contact, that, although its existence was recognized, it could not be isolated until Moissan accomplished the feat in 1886.   On the other hand, argon, although present in the atmosphere to the extent of one per cent, escaped detection until 1894, perhaps because of its great inactivity, as all of the many attempts to make it enter into combination have been so far (1899) without established success.   Oxygen is the most universally reactive, forming compounds with all the other elements, except fluorine, argon, and helium.

The *heat disturbance* per gram of element in combining **199** with oxygen ranges from 34,200 calories for hydrogen in the formation of water, to −1540 calories for nitrogen in the formation of nitric oxide; or if the comparison is made per combining weight, which is probably more suitable, the values are 143,900 calories for 24 grams of magnesium, and −21,600 calories for 14 grams of nitrogen.

1. HYDROGEN

Symbol H.—Comb. wt. 1

History.—Hydrogen was studied and for the first time identified by **200** Cavendish in 1766, although Paracelsus in the sixteenth century noted the production of an inflammable gas by the action of acids on metals.

In 1781 Cavendish showed that it is a constituent of water.   Its name signifies water-producer, and was given it by Lavoisier.

Natural occurrence.—It is found uncombined, but only in **201** small quantities, in volcanic gases, in the gas from oil wells, and sometimes in meteorites.   On the other hand, as a constituent, hydrogen is both very abundant and widely distributed. It forms one ninth of all water, and is contained in organic matter of both plant and animal origin, and also in all acids.

202   **Preparation.**—1. By the passage of the electric current through slightly acidulated water (electrolysis), by which hydrogen and oxygen are set free.
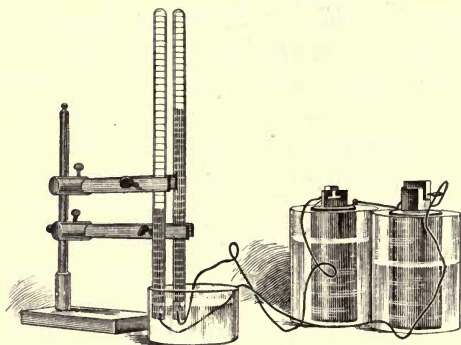
Fig. 2.—The electrolysis of water. Showing how the current from the electric battery is passed through acidulated water, and the gases collected in the gasometric tubes. The ratio of volumes is 2 : 1.

2. By the action of some dilute acids on some metals, a salt being the second product. Of acids, hydrochloric and sulphuric are the most available, and for the metals, zinc, iron, magnesium, and aluminium are commonly used.

3. By the action of sodium or potassium hydroxide in solution on some metals, usually zinc or aluminium. In this reaction, zinc or aluminium oxide is produced and combines with the hydroxide, forming a soluble compound.

4. By the action of a few metals, practically sodium and potassium, on water at ordinary temperature, the metal being oxidized by the oxygen of the water. The metallic oxide in turn combines with water, and the soluble hydroxide is formed.

5. By the action of some metals, for example iron, at a red heat on water vapor, an oxide of the metal being the second product.

6. By the action of carbon at a high temperature, white heat, on water vapor. The carbon is oxidized to carbon monoxide, a gas, so that a mixture of this substance and hydrogen is obtained. This mixture is made on a commercial scale and is known as " water-gas."

These reactions are expressed in equation form as follows:

1. $H_2O = 2H + O$
2. $Zn + 2HCl = 2H + ZnCl_2$
3. $Zn + 2NaOH = 2H + Na_2ZnO_2$ (or Na_2O,ZnO)
4. $Na + H_2O = H + NaOH$
5. $3Fe + 4H_2O = 8H + Fe_3O_4$
6. $C + H_2O = 2H + CO$.
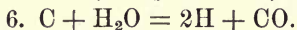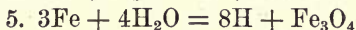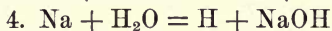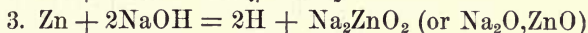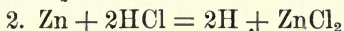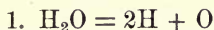
Physical properties.—Hydrogen is a gas without color, **203** taste, or odor. The odor usually noted is due to impurity coming from the metal or the acid. It is the lightest of known substances, 14.4 times lighter than air. One liter of it weighs 0.0899 of a gram at 0° and 760 mm. Being specifically very light, it also possesses high *diffusibility* **203**/1 —that is, the power of mixing with other gases, and of passing through a porous wall. This property varies inversely as the square root of the density, so that hydrogen diffuses nearly four times as rapidly as air.

It is but slightly *soluble* in water, 100 volumes dissolving **204** 1.84 volumes of the gas at 760 mm. and 20° C.

Occlusion.—Some metals show the property of absorbing hydrogen. Conspicuous for this is palladium, which absorbs more than nine hundred times its volume of gas. Platinum **205** and iron show the property in less degree. The hydrogen of meteorites is thus occluded by the iron. The gas absorbed is given up again at a high temperature. It is not improbable that chemical action plays some part in occlusion.

Liquefaction.—At a pressure of 180 atmospheres and a **206** temperature of −205°, hydrogen condenses to a clear, transparent liquid whose density is fourteen times less than that of liquid water, and whose boiling point, under atmospheric

pressure is, $-238°$, the lowest temperature yet reached (Dewar, 1898).

207   Chemical properties.—Hydrogen has no action on litmus. It burns in air or in oxygen with a pale-blue, almost invisible flame, forming water, and liberating 34,200 calories per gram, which is more heat than any other substance gives on burning. A mixture with air may be violently explosive, as already stated. At a high temperature, it reduces many metallic oxides—that is, deprives them of oxygen—for example, copper, silver, and even iron oxides. With chlorine it combines even explosively, and it also forms compounds with bromine, iodine, carbon, nitrogen, phosphorus, sulphur, and the metals, potassium, sodium, and others.

208   *Nascent state.*—Hydrogen and also other substances show, at the instant of liberation from a compound, a higher degree of chemical activity than after the separation has taken place. This is called the nascent state. Nascent hydrogen is able to deprive potassium permanganate of a portion of its oxygen, a power which hydrogen in mass does not possess.

208/2   As a *theoretic explanation* of this fact, it has been suggested that in the nascent state the substance may be in the atomic condition; the atoms, not having come together into molecules, may possess more chemical energy than after they are united.

209   Hydrogen is not *poisonous*, but it is incapable of sustaining life. It may be inhaled for a short time, and in this circumstance it gives a shrill tone to the voice.

2. LITHIUM

Li.—6.97

210   *History.*—The oxide of lithium was discovered in 1817, but the element was not separated until 1855.

211   **Natural occurrence.**—It is not found free, and only in small quantities as a constituent, but in a great variety of

compounds; in many minerals, in particular one of the varieties of mica; in some mineral waters and in the sea; in some soils; in some plants—e. g., tobacco, beets, sugar-cane; in milk, and in the human body; in some meteorites, and in the atmosphere of the sun.

Preparation.—It is prepared by the electrolysis of its **212** fused chloride.

Properties.—It is a metal like silver in color and luster, **213** but softer than lead. With a specific gravity of 0.59, it is the lightest of solids. It melts at 180°.

It tarnishes in the air by oxidation, and at a tempera- **214** ture above 180° it burns brilliantly. It decomposes water at ordinary temperature, liberating hydrogen and forming the oxide, which is Li_2O. This, in turn, combines with water, forming the hydroxide, LiOH, which is soluble and is a strong base, resembling sodium hydroxide.

The metal combines with hydrogen, carbon, and nitro-gen, forming respectively the hydride, LiH, the carbide, Li_2C_2, and the nitride, Li_3N. These react with water on contact, forming respectively hydrogen, acetylene, C_2H_2, and ammonia, NH_3. Lithium reacts with fluorine and with chlorine violently, and the metal, and its oxide and its hydroxide, react with hydrofluoric acid and with hydro-chloric acid, in each case forming the fluoride, LiF, or the chloride, LiCl. Lithium colors the Bunsen flame a bright crimson.

The alkali metals.—It is customary and convenient to **215** classify in one group or family those metals which de-compose water at ordinary temperature and form soluble oxides and hydroxides, which act as strong bases, and whose salts are generally soluble. They are called the *alkalies*, and lithium, sodium, and potassium are the members of the group which are described in this course. The ammonium compounds are also classified with these.

3. GLUCINUM or BERYLLIUM

Gl. or Be.—9.0

216   *History.*—The oxide of glucinum was discovered in 1798 in the mineral, *beryl*, but the element was not separated until 1828, and then by Wöhler. It was first named *glucinum*, signifying sweet, from the property of its salts, and later *beryllium.*

217   **Natural occurrence.**—It is not found free, but is found in some minerals, particularly beryl, of which emerald and aquamarine are varieties. In these it is combined with oxygen, silicon, and aluminium.

218   **Preparation.**—It is obtained by heating its chloride with sodium.

219   **Properties.**—It is a white metal. Its melting point is lower than that of silver. Its specific gravity is 1.85 at 20° (Ramsay). When in compact condition, it oxidizes only superficially in the heat of the blowpipe. If finely divided, it burns brilliantly when heated in the air. It does not decompose water below 100°. Its oxide is GlO, a white powder, insoluble in water, which, however, forms a hydroxide with water, GlO_2H_2. The latter is insoluble in water, and acts as a base primarily. The metal, the oxide, and the hydroxide react with hydrochloric acid, forming the soluble chloride, $GlCl_2$. They also dissolve in sodium and potassium hydroxides, forming glucinates, compounds in which glucinum oxide seems to act as acid to the alkali base. Glucinum forms a hydride (GlH?), and a carbide (Gl_4C_3?).

4. BORON

B.—10.86

220   *History.*—Boron was first separated as an element about 1808 by Gay-Lussac, Thénard, and Sir Humphry Davy, but its compound, borax, was known many years earlier.

221   **Natural occurrence.**—It has not been found uncombined, but its oxide, combined with water—that is, boric acid—oc-

curs in the water of some volcanic regions, notably in Tuscany, also as a mineral; and the sodium salt of this acid, known as borax, is found abundantly in California, and is a familiar article of commerce.

Preparation.—Boron is best prepared by heating its **222** oxide, B_2O_3, with magnesium, which combines with the oxygen and liberates the boron.

Properties (according to Moissan, 1895).*—Thus pre- **223** pared, it is a brown amorphous powder, of neither taste nor odor, insoluble in all ordinary solvents, and infusible, but probably volatile without fusion in the electric arc. Its specific gravity is 2.45.

It forms with hydrogen the compound BH_3.† Heated **224** in air to 700°, it burns readily, forming the oxide B_2O_3, and in oxygen it burns with intense brilliancy. It combines directly with fluorine, with chlorine, and with bromine, forming BF_3, BCl_3, and BBr_3; with carbon, B_6C and B_2C_2; with sulphur, B_2S_3; and with some metals—e. g., iron, BFe, and aluminium and magnesium. At 1230° it combines with nitrogen, forming BN. Above red heat it decomposes water violently. It also removes oxygen from many metallic oxides. Indeed, it is a most active reducing agent.

Boron oxide, B_2O_3, is the only compound with oxygen. It **225** is formed by direct union with oxygen, and also by driving off the water of boric acid at a red heat. It melts to a glasslike mass, and volatilizes only at the highest temperature. It dissolves in water, at the same time combining with water, forming a hydroxide commonly called *boric acid*. This may be crystallized from water in white shining scales. It is also liberated from the borates by sulphuric or hydrochloric acid. It is soluble in alcohol, and imparts **226** to the alcohol flame a characteristic green color. This is a common test for its identification.

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* Annales de Chemie et de Physique (7), vi, 1895.
† Sabatier, Comptes rendus, 1891.

227   Boron oxide combines with water in three proportions, forming acids, thus:

$$B_2O_3 + 3H_2O = H_6B_2O_6 = 2H_3BO_3,$$ named orthoboric acid.
$$B_2O_3 + H_2O = H_2B_2O_4 = 2HBO_2,$$ named metaboric acid.
$$2B_2O_3 + H_2O = H_2B_4O_7,$$ named tetra or pyroboric acid.

228   Borax is the sodium salt of the pyroboric acid, $Na_2B_4O_7$, crystallizing with $10H_2O$, and showing a slight alkaline reaction. The fused salt, and the boric oxide itself, dissolve many of the metallic oxides, in many instances forming transparent glasslike substances of characteristic colors. These are used for identification in the borax-bead tests. Borax is used also for cleaning metallic surfaces preparatory to soldering, for glazing porcelain, in the making of glass and of soap, also as a drug, and as an antiseptic—that is, as a preventive of putrefaction and fermentation.

Boron oxide in the compounds mentioned and in others clearly acts as an acid-forming oxide. But it seems to be capable of acting also as a feeble base. It reacts with hydrofluoric acid, forming a fluoride, as do metallic oxides, although this compound is a gas and readily decomposed by water:

$$B_2O_3 + 6HF = 2BF_3 + 3H_2O.$$
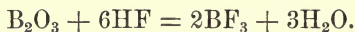
It combines with phosphoric acid, H_3PO_4, forming a phosphate, BPO_4, in which the boron apparently acts as a base.

5. CARBON

C.—11.91

234   Uncombined carbon exists in three allotropic forms—diamond, graphite, and amorphous carbon of which charcoal is one variety.

Diamond

235   **History.**—Diamond, the transparent crystallized form of carbon, has been known and prized as a gem for ages. It

was at one time regarded as a variety of rock crystal (silica). Sir Isaac Newton surmised that it might be combustible because of its high refractive power, like that of turpentine and other substances which were known to burn. In 1695 two Italians proved the correctness of this suggestion by burning a diamond in the focus of a powerful burning-glass. Later, about 1766, Dorcet showed that when heated in a hermetically sealed vessel the diamond was unchanged. Then Lavoisier, in connection with his famous investigation of combustion, burned the diamond in a closed vessel with air and proved the formation of carbon dioxide. Then, by the work of several investigators, between 1796 and 1800, it was proved that equal weights of charcoal, graphite, and diamond gave equal weights of carbon dioxide. Finally, Sir Humphry Davy, in 1814, using the same burning-glass that was used by the Italians in 1695, showed that no water was produced in burning diamond, and therefore that this substance contains no hydrogen. He went still further, and, combining with lime the carbon dioxide made by burning diamond, he produced calcium carbonate, which in turn he reduced by heating with potassium. This yielded him a black powder which burned like ordinary charcoal. (History according to Roscoe.) Thus the evidence became complete that diamond is simply pure crystallized carbon.

Diamonds have been found in the East Indies, since **236** 1727 in Brazil, and since 1867 in South Africa; to a less extent elsewhere. Its presence in a meteorite has been noted.

Properties.—The diamond is a natural crystal, which, **237** however, is cut and polished to serve as a gem. It is transparent, sometimes colorless, sometimes tinted green, brown, or yellow, sometimes black. Its luster and high refractive power give it brilliancy as a gem. In hardness it is not exceeded by any known substance, and is equaled by only one

or two. Its specific gravity is 3.5 at least. It is a poor conductor of heat and electricity.

238   It may be heated in hydrogen to 1,200°, white heat, without change ; but when thus heated in the electric arc it swells, and becomes black like coke or graphite. When heated in oxygen to 700° or 800° it burns, leaving only a minute ash. It reacts with no substances at ordinary temperature, and even at high temperature with only a few. Heated to 1,000°, it is acted upon by sulphur, giving carbon disulphide ; also by sodium or potassium carbonate, giving carbon monoxide. Melted iron and melted platinum dissolve it and combine with it, and on cooling give it up as graphite (according to Moissan, 1896).

239   **Uses.**—Some of the most famous diamonds of the world are in the possession of states or sovereigns. The Regent diamond weighs 136 carats, or about 27.9 grams (a carat equals 0.205 of a gram), and is valued at $625,000. Diamonds of inferior quality are used to cut and polish diamonds and other gems, and as points of tools for boring rocks and for cutting glass.

240   *Carbonado* and *anthracitic diamond* are forms of impure carbon, approaching the diamond in properties, but of less density and hardness than the true diamond.

241   **Artificial diamond.**—Of the many who have attempted to prepare the real diamond artificially, Moissan was the first to succeed and to prove his success beyond question. The account of this work was published in 1896. His procedure was to saturate molten iron (silver also was used in place of iron) with pure carbon in the electric furnace at the enormous temperature of about 3,500°, which greatly increases the solvent power. This mass was then suddenly cooled by plunging it into water, or sometimes into melted lead whose temperature was about 325°. Under these conditions a solid crust is formed while the interior is still molten, and as iron expands on solidifying, the liquid portion is thus put under great pressure. When sufficiently cool, the metal and the excess of carbon (now graphite) were

dissolved by reagents, and minute crystals or crystalline fragments were obtained, which were sometimes black, sometimes transparent, had the hardness and specific gravity of the diamond, and consisted of pure carbon, in fact were minute but real diamonds. The great pressure was found to be an essential condition, and without it the carbon appeared simply as graphite.

One of his samples measured 0.57 mm., and among them **242** were reproduced many of the peculiar features seen in natural diamonds. The remarkable results of Moissan's ex-
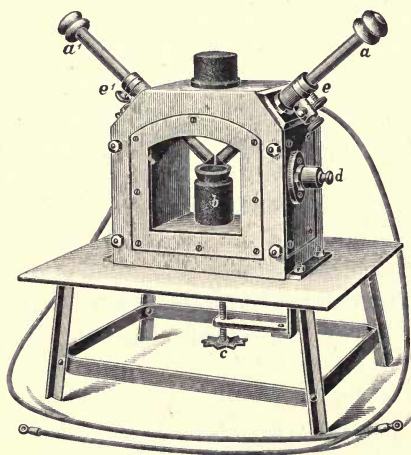
FIG. 3.—One form of the electric furnace for research work ; *e* and *e¹*, the poles by which the current enters and leaves; *b*, the crucible in which the material is heated by the arc; the sides are figured open in order to show the arrangement.

periments give much force to his suggestion that the natural diamond has probably been formed in the deeper layers of the earth's crust, where enormous pressure exists, and that it is not unlikely that iron may have been the solvent. Indeed, minute transparent diamonds have been found in the midst of meteoric masses of iron.

Graphite

243   Graphite, the second allotropic form of carbon, called also *plumbago* and *black lead*, is found in considerable quantities and in many places, notably in England, Bohemia, Siberia, Ceylon, California, Massachusetts, New York, and Michigan.   Its presence in meteoric iron has been noted.

244   It exists in crystallized condition.   In color it is black or grayish black, and sometimes of almost metallic luster. It is so soft that it makes a black mark on paper and leaves a stain on the finger, and it is soapy to the touch.   It differs from the diamond in lower specific gravity, about 2.0–2.25, and in igniting in oxygen below 700°; also in yielding to oxidation by a mixture of strong nitric acid and potassium chlorate, whereby a colored, green or yellow, crystalline oxide is obtained.   It is also a good conductor of heat and of electricity.   At low-red heat it does not decompose water nor oxidize in air.   Natural graphite leaves more ash than diamond.

245   It is made artificially by heating diamond, or the many varieties of charcoal, to the high temperature of the electric arc ; also by dissolving carbon in many of the metals, melted at a high temperature.   When the metal cools, the graphite separates in crystals.

246   **Uses.**—The substance finds use as material for crucibles in which metals are melted, both on a large and a small scale ; as material for which the so-called lead of pencils is made, whence its name signifying *to write ;* as conducting material in the process of electroplating ; and as lubricant.

Carbon as Constituent

247   Besides diamond and graphite, the native forms of the element, carbon as a constituent is found in the air and in natural waters as carbon dioxide ; in all the carbonates, such as marble, limestone, chalk ; in petroleum and in "natural gas" ; as the fundamental constituent of all plant and animal structures ; and in all varieties of coal.

Amorphous Carbon

Preparation.—From the fully oxidized compounds of **248** carbon—that is, carbon dioxide and the carbonates—carbon can be obtained only by removing the oxygen with which it is combined. This may be done by heating with such substances as boron and magnesium. From substances of plant and of animal origin, in which it is combined with hydrogen, and often with oxygen and nitrogen, but in which it is not fully oxidized, it is obtained generally by *charring* or by dry distillation—that is, by heating without sufficient air to cause complete combustion. The constituent hydro- **249** gen burns the more easily ; therefore the carbon predominates in the residue. The varieties of carbon thus obtained depend on the various sources and the methods of making. They are all quite impure as commercial articles, but they are alike in being soft, amorphous, black or brown, of specific gravity less than 2.0; easily oxidized by nitric and chromic acids ; and some of them take fire in oxygen as low as 375°.

Lampblack is one of the purest varieties. It is the black **250** deposit familiarly known as soot, from the flame of carbon-containing fuel, made smoky by incomplete combustion. It is used in making inks and paints.

Gas carbon is deposited from the gases in the retorts in **251** which illuminating gas is made. It is harder and denser, and, being a good conductor, has been used in making battery plates and the poles of electric lamps.

Bone black or *animal charcoal* is the residue obtained **252** by charring bone, blood, and other refuse of animal origin. It is very porous and absorptive, and is used largely to decolorize sirups in sugar refining.

Coke is the solid residue from the distillation of coal **253** and is used extensively as fuel, especially in obtaining metals from their oxides.

Wood charcoal is the solid residue from the distillation **254** of wood. When wood is heated to high temperature with

little or no air present, water is eliminated, also a gaseous mixture which burns with luminous flame and contains carbon and hydrogen; a liquid also is obtained which has acid reaction, and contains creosote and other tarlike substances of which carbon is a constituent. The greater part of the carbon, a little of the hydrogen, and all of the ash are left

254/1 in the solid residue, which is charcoal. This retains, more or less, the structure of the wood; is black or brown, soft, brittle, and very porous and absorptive. It floats on water only until the air is expelled from its pores. Its properties vary considerably with the kind of wood and the temperature of distillation. It is able to absorb from 90 to 170

255 times its own volume of ammonia gas, about 50 volumes of hydrogen sulphide, from 10 to 18 volumes of oxygen, etc. This property leads to its use for the purpose of absorbing the offensive and harmful gases which accompany putrefaction, also to purify the air in the sick-room, etc. By virtue of the same property, it removes

255/1 many substances from solution, and hence its extensive use as filtering material—e. g., to remove the coloring matter from sirups on a large scale; also, to filter water for drinking. In some instances it seems to absorb physically, and the substances may be recovered from the charcoal; in others it brings about chemical changes within its pores, especially oxidation. Thus, when used as filtering material, it loses its effectiveness in time, and this may be restored by exposure to air, which renews its supply of absorbed oxygen.

Common Properties

256   It is seen, therefore, that the element *carbon*, as to many of its properties, varies in a most remarkable manner in its different conditions. In all its forms it was regarded as entirely infusible and non-volatile until Moissan showed that at the highest temperature of the electric furnace (3,600°) it volatilizes without melting, and condenses as
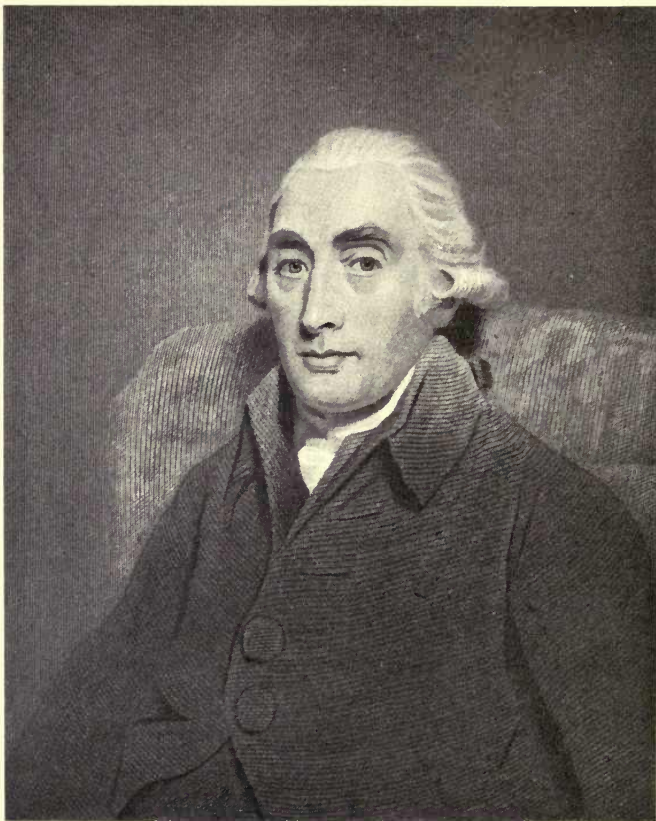
JOSEPH BLACK
B. Bordeaux, 1728.   D. Edinburgh, 1799.
(See Nos 259, 577.)

graphite. It is insoluble in all ordinary solvents, but dissolves in many of the metals which melt at high temperature.

In its *chemical reactions* also carbon is most remarkable. **257** At ordinary temperature it is almost completely inactive, although in amorphous condition it does yield to powerful oxidizing agents below 100°. It must be heated to several hundred degrees before it combines with the oxygen of air, but when heated it is able to take oxygen from many compounds. This leads to the use of charcoal and coke on an enormous scale in the industrial processes of obtaining the metals from their native oxides (i. e., metallurgy).

In the high temperature of the electric arc, carbon combines directly with hydrogen, forming acetylene, C_2H_2. It **258** forms innumerable other compounds with hydrogen, but not by direct action between the two elements. It also combines at high temperature with lithium, forming a crystallizable compound, Li_2C_2; likewise with many other metals—e. g., sodium, potassium, magnesium, and calcium, forming also *carbides ;* with boron, forming B_6C, crystalline, and rivaling the diamond in hardness; with nitrogen, forming the intensely poisonous *cyanogen*, C_2N_2; with fluorine; with chlorine, CCl_4; with silicon, forming *carborundum*, CSi, very hard and used like emery in grinding and polishing ; and with sulphur, CS_2.

5a. *Carbon Dioxide, CO_2*

History.—Van Helmont (1577–1644) noted that a substance which **259** he named "gas sylvester" was produced by fermentation, by decay, and by combustion, and was found in certain natural caves. He obtained it by the action of acids on carbonates, and observed that it suffocated animals and extinguished flame. Black (1755) called it "fixed air." Bergmann studied it in 1774, and named it "acid of air." But Lavoisier first explained its chemical relationship (Roscoe).

Natural occurrence.—It is a normal constituent of the **260** atmosphere to the extent of about 4 volumes in 10,000. It

is a product of ordinary combustion, of the respiration of animals, of fermentations, and of organic decay. It issues from the earth in some volcanic regions, and is dissolved in most natural waters. As a constituent of carbonates it occurs abundantly in the soil and in extensive layers of the earth's crust.

261 **Preparation.**—It is commonly prepared by the action of acids on carbonates, or by decomposing calcium carbonate by heat, or by burning carbonaceous matter.

262 **Properties.**—It is a gas at ordinary temperature, without color, and with little, if any, odor. It is one and a half times heavier than air, and twenty-two times heavier than hydrogen. At normal pressure and at 20°, 100 volumes of water dissolve about 90 volumes of the gas. The quantity dissolved is greatly increased by pressure, but when the pressure is removed the gas escapes with effervescence. It condenses at 10°, under a pressure of about 36 atmospheres, to a clear, colorless liquid, whose boiling point is $-78°$, and freezing point nearly the same. It freezes by its own evaporation to a white, snowlike solid. Liquid carbon dioxide, stored in strong iron cylinders, has become a commercial article.

263 Carbon dioxide is not combustible, and it extinguishes all ordinary combustion and destroys animal life. A few substances—boron, sodium, potassium, and magnesium—when heated, burn in it, depriving it of its oxygen. Red-hot carbon also decomposes it, forming carbon monoxide, and it is partly decomposed into this substance and oxygen by a temperature of 1,300°. A candle ceases to burn in air containing 4 per cent of carbon dioxide, although the oxygen is far from exhausted. An animal can tolerate such air for only a short time; hence the method of testing by a lighted candle the air of wells, caves, mines, or similar places where the gas may accumulate by reason of its high specific gravity. Fatal accidents have happened from failure to take precautions before entering such

places. Miners, who have frequently to encounter it, call it "choke damp." Air containing so little as 0.2 per cent is said to have injurious effect if long respired.

In dissolving in water the gas probably combines with **264** it to slight extent, forming dilute *carbonic acid*, since the solution feebly reddens litmus, whereas the dry gas does not. The acid is very unstable, however, easily changing into the original constituents; but if a soluble base is present the salt is formed, and this is quite stable. The salts are called *carbonates*, and their composition implies an acid **265** of the formula H_2CO_3. Those of the alkali bases, like sodium carbonate, are soluble. The others are generally insoluble. Upon this fact depends the usual test for carbon dioxide, namely, the turbidity produced in lime-water (calcium hydroxide).

Relation to life.—In relation to living things, carbon **266** dioxide plays a most important part. As has been already stated, carbon is the fundamental element of both the plant and the animal organism. The carbon dioxide of the atmosphere constitutes an essential food of plants. From this and water it builds up much the greater portion of its substance. Absorbing the gas by the extensive surface of its leaves and other green parts, and aided by the energy of sunlight, associated in some way with the green coloring matter of the leaves (called *chlorophyll*), the plant is able to remove a part of the oxygen, rejects it, as it were, and passes back to the atmosphere a quantity of it nearly equal to that contained in the carbon dioxide absorbed. From the residue it builds up the wood, starch, sugar, and many other **267** substances which constitute its entirety. Upon these, or a part of them, the animal depends for his food, consuming some, such as starch and sugar, and from them not only building his body substance, but deriving his energy by the chemical changes which they undergo. These changes result ultimately in the complete oxidation of a part of the carbon to carbon dioxide and the rejection of this from the

lungs as a waste product, which is thus returned to the atmosphere to serve again as food for the plant.   In addition
268   to this, man utilizes the deoxidized carbon of the plant in the form of wood, or, as will be seen later, in the form of coal, as the chief, practically the only, source of artificial heat, and hence of the mechanical energy which is dependent on it.   One of the marvelously delicate adjustments of nature is seen in the fact that the proportion of carbon dioxide in the atmosphere, considering it as a whole, has not appreciably changed within the history of observation, and probably not during the existence of the human race ; and this, in spite of the immense quantities of the substance thrown into the air by respiration, by combustion, and by decay, and drawn out of it and stored up in the enormous mass of plant products.

5b. *The Carbonates*

269   The carbonates occur frequently and abundantly as minerals—e. g., iron carbonate, magnesium carbonate, and, most abundant of all, calcium carbonate in its several varieties, namely, chalk, limestone, marble, and calcite.   Sodium carbonate and potassium carbonate are manufactured and used in large quantities.

270   The carbonates in some instances are formed by the combination on contact of carbon dioxide and basic hydroxides.   The formation of sodium carbonate and calcium carbonate in this way has already been cited.   Calcium oxide, CaO, and one or two other oxides combine directly with carbon dioxide, liberating much heat.   Non-alkali carbonates, being insoluble, are precipitated, if they form at all, by mixing solutions of non-alkali salts and alkali carbonates. Some bases, however—e. g., aluminium hydroxide—do not combine with carbonic acid in the presence of water.

271   There are two types of carbonates—those in which the metal has displaced the whole of the acid hydrogen, and those in which only one half is displaced.   The first are

the *normal,* the second, the *acid* carbonates. Of the first type are sodium carbonate, Na_2CO_3, and calcium carbonate, $CaCO_3$; of the second is sodium acid carbonate, or bicarbonate, $NaHCO_3$. The acid carbonates of the alkalies only are well defined. The acid carbonates of calcium, magnesium, iron, and others are supposed to be formed when the normal carbonates are dissolved by excess of carbon dioxide, but they decompose so easily that they can not be obtained out of solution, and heating the latter causes the precipitation of the normal carbonates.

5c. *Carbon Monoxide, CO*

This, the second of the two oxides of carbon, is produced **272** in circumstances which do not permit the complete oxidation of carbon—e. g., insufficiency of oxygen; also when carbon dioxide passes over red-hot carbon or metals. It is a gas without odor or color. Its specific gravity ($H = 1$) is 13.93, nearly the same as air. One hundred volumes of water dissolve only about two of the gas. Under great pressure and low temperature it condenses to a liquid which boils at $-190°$ and freezes to a white solid at $-199°$. It burns with a pale-blue flame to carbon dioxide. The flickering **273** blue flame that is frequently seen over a bed of glowing coals is due to this substance, formed from the dioxide which passes upward through the hot mass, is deoxidized, and burns as the monoxide when it comes to abundant air. The monoxide has no action on litmus, and forms no acid with water. It is intensely poisonous, combining with one of the constituents of the blood, and fatally modifying its normal action. The not infrequent deaths through exposure to the gas from coal stoves and furnaces are due to this substance, which is the more dangerous from the fact that it has no odor and its stupefying effects give no alarm. One per cent in the air may cause death (Parkes). It is present in common illuminating gas.

5d. *The Hydrocarbons*

274   This is the name applied to the compounds of carbon and hydrogen. They are many in number and varied in kind, and reveal another remarkable property of this element, carbon.

275   **Methane** is the simplest of the group; its formula is CH_4. It occurs, first, as a product of the decay of plant substances—for example, in stagnant water and marshes, where bubbles of gas may be seen coming to the surface, or may be caused to rise in quantity by stirring the sediment at the bottom (whence its name "marsh-gas"); second, in coal mines, where it is known as "fire-damp," and causes many terrible explosions; third, associated with petroleum, and as the chief constituent of the so-called "natural gas." As an artificial product, it is the larger part of the gas produced in the distillation of wood and of coal—i. e., illuminating gas. For laboratory purposes it is conveniently

276 prepared by the dry distillation of sodium acetate mixed with a strong base such as lime. It is formed also by the action of water or acids on some of the metallic carbides, at ordinary temperature; for example, aluminium carbide, thus,

$$C_3Al_4 + 12H_2O = 3CH_4 + 2Al_2(OH)_6;$$
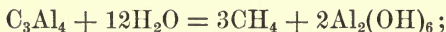
also by the reaction which is expressed in the following equation:

$$2H_2S + CS_2 + 8Cu \text{ (red hot)} = CH_4 + 4Cu_2S.$$
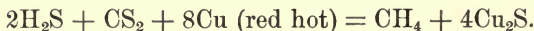
277   Methane is a gas without color or odor, and nearly insoluble in water. Its specific gravity is 7.95 ($H = 1$). It condenses to a liquid which boils at $-164°$, and solidifies at about $-186°$. It burns with a pale, almost non-luminous flame to carbon dioxide and water.

278   Closely allied with methane are *ethane*, *propane*, and *butane*, which have the formulas, respectively, C_2H_6, C_3H_8, and C_4H_{10}. In composition they differ from each other by

the constant difference CH_2. Substances thus differing in composition and possessing a family or group resemblance in properties are said to be *homologous*, and the series is called a homologous series. The one of which methane is the first member is called the *paraffin series*. They may be represented by the general formula $C_nH_{(2n+2)}$. One is known in which $n = 60$. As the proportion of carbon increases beyond $n = 4$ they become liquids, and finally solids at ordinary temperature.

Ethylene, C_2H_4, is the first member of a second series of **279** hydrocarbons known as the ethylene or *olefin series*. It, too, is a product in the dry distillation of wood and coal. It is also formed by the action of acids on some of the metallic carbides, and in the laboratory usually by heating a mixture of strong sulphuric acid and alcohol. It is a colorless gas, almost insoluble, condensable to a liquid which boils at $-105°$. It burns with a bright flame, and is the chief light-giving constituent of illuminating gas. Others of the series are *propylene*, C_3H_6, and *butylene*, C_4H_8. Their general formula is C_nH_{2n}, and the increment of composition is CH_2, as in the paraffins.

Acetylene, C_2H_2, is the first member of the third series, **280** and is of special interest. Reference has already been made to the fact that this substance is produced by the direct union of the elements at the temperature of the electric arc, and that it is endothermic (see Nos. 54 and 58, Part I), with a heat of formation of $-47,600$ calories. It occurs also as a product of the distillation of wood and coal, and hence in coal gas. It is formed, too, when coal gas burns with insufficient air; thus when the gas becomes ignited at the base of the Bunsen burner the odor, very quickly noted, is that of acetylene. Another method of making it which has attracted much attention of late is by the action of water on the carbides of such metals as have a strong tendency to seize on the oxygen of water, particularly calcium carbide, CaC_2. This substance is produced by the reaction of lime,

CaO, and charcoal at a very high temperature, which has become easily available since the introduction of the electric arc for heating. When calcium carbide and water are brought in contact at ordinary temperature, reaction takes place as expressed in the equation

$$CaC_2 + H_2O = CaO + C_2H_2.$$
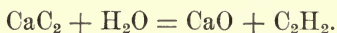
The carbide has become a commercial article, and comparatively cheap, and it is proposed to supply it as a source for illuminating gas. It has also been proposed to supply the gas itself under pressure in transportable tanks.

281   Acetylene is a gas without color, but of marked and peculiar odor. It is soluble in its own volume of water. Its specific gravity is 13.1 (Moissan). It liquefies under a pressure of forty-eight atmospheres at 0°. It is poisonous if inhaled in considerable quantity. Accompanying its endothermic character is its high chemical activity. Brought in contact with a solution of silver salt, it yields a white precipitate, and with cuprous salt a red precipitate—a good qualitative test. These substances have the composition Ag_2C_2 and Cu_2C_2 respectively, yield acetylene by treatment with acid, and when dry, are very explosive. Acetylene, when pure and burned freely in the air, shows a luminous but smoky flame; but when mixed with air in a suitable burner, it yields a very brilliant white light. The heat given out by the combustion of carbon and hydrogen is of course greatly increased by the decomposition heat of

281/1 acetylene. Indeed, the gas itself may be explosive under certain conditions; for whatever would cause its decomposition into carbon and hydrogen would cause a sudden liberation of energy, although the volume of gas produced would not exceed the original volume. Under atmospheric pressure it does not readily explode, and only by detonation; but under twice the atmospheric pressure it may be violently exploded. In England it is reckoned as subject to the law concerning explosives, if under a pressure of more

than 1.05 atmospheres (i. e., atmospheric pressure plus about 20 inches of water column); similarly in Germany, if under a pressure of more than 1.1 atmospheres; and in France, if under more than 1.5 atmospheres.*

281/2 Another peculiar feature of its chemical activity is its property of combining with itself, which is provoked simply by heating, and results in the formation of two volumes of benzene, C_6H_6, from six volumes of acetylene. This is called *polymerization* (see Nos. 85/1, 86, and 179, Part I). Acetylene combines also with hydrogen, forming ethylene, C_2H_4, and ethane, C_2H_6. There are only a few homologues of acetylene known. Their general formula is $C_nH_{(2n-2)}$.

282 One other series should be mentioned, although it does not by any means exhaust the list. This is the series of which the first member is *benzene*, C_6H_6, and the second *toluene*, C_7H_8. Their general formula is $C_nH_{(2n-6)}$. They are derived from coal tar, and have a large industrial importance. Benzene is a clear, oil-like liquid, of boiling point 80.5°.

283 The hydrocarbons, therefore, are extremely numerous and in themselves highly interesting substances. But more than this, they are the parent substances, so to speak, from which are derived, by definition at least, the almost innumerable substances called *organic;* so called because it was formerly thought that their production was dependent on vital energy. This conception having changed, they are now more fitly designated as the hydrocarbons and their derivatives, and they constitute the subject-matter of " Organic Chemistry." This branch is so extensive that its literature is more voluminous than that of all the rest of chemistry put together.

5e. *Flame*

See Nos. 284–292, Part II.

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* Chemical News, October 8, 1897.

5f. *Petroleum*

293   Petroleum is a liquid mineral which issues from the earth, or is brought to the surface by boring, in many parts of the world. The most important sources are in Pennsylvania, New York, Ohio, West Virginia, and some other districts in this country; in Ontario, Canada; in Russia, on the Caspian; in Burmah, India, and Japan. Closely related to petroleum is the natural gas which likewise issues from the earth. "Burning springs, as they have been termed, have been known from the earliest historical times. Those of Baku, on the Caspian, are supposed to have been burning as early as the sixth century B. C., and to have been a sacred shrine of the Persian fire-worshipers. The Chinese have employed natural gas for centuries in their salt mines as a source of light. In the United States it was employed in 1821 at Fredonia, New York, for illuminating purposes; and for fifty years past it has served as the fuel for the evaporation of brine at the salt-wells of the Kanawha Valley, West Virginia." (Sadtler.) Natural gas to the extent of about ninety per cent is made up of methane and a small quantity of one or two of its homologues.

294   Crude petroleum varies somewhat in character. That of Pennsylvania is generally dark, greenish black in color, and red by transmitted light. It is lighter than water, and is essentially a mixture of paraffin hydrocarbons, some of the gaseous members and some of the solid being dissolved in the liquid. Its refining consists of distillation and treatment with sulphuric acid, and sometimes dilute alkali, to remove those substances which are objectionable by reason of their odor, and which frequently contain sulphur. The products of petroleum come into commerce under various names, the following among them:

PARAFFINS.	Name.	Boiling point.	Uses.
Below C_5 .	Cymogene......	$0°$	Manufacture of ice.
C_{4-5}	Rhigolene......	$18°$	Anæsthetic in medicine.
C_{5-6}	Petroleum ether.	$40°–70°$	As a solvent and in gas-making.
C_{6-7}	Gasolene........	$70°–90°$	As a solvent and in gas-making.
C_{7-8}	Naphtha, or ligroine	$80°–120°$	As a solvent and as fuel.
C_{8-9}	Benzine........	$120°–150°$	As a solvent.
C_{10-16}	Kerosene	$150°–300°$	Illuminating oil.

295   Other liquid portions find use as lubricating oils; and the solids of lowest melting point, $40°–50°$, $n = 21–23$, appear as vaseline; and of melting point from $51°–57°$, $n = 22–28$, as the white paraffin which is

familiar in the laboratory. The latter is used largely in candle-making, in finishing calicoes and similar goods to give a luster to the surface, in waterproofing paper, in making Swedish matches, and in extracting perfumes from flowers. (Mostly according to Sadtler.)

296 The presence in kerosene of the easily volatile and inflammable members of the series must make its use as an illuminating oil more or less dangerous. The public is protected in many countries by legislation making it unlawful to sell for such purpose an oil which, below a specified temperature, gives off vapor enough to be ignited. This temperature is called the *flashing point*, and it is determined for a given sample by heating in a suitable vessel until by trial the vapor above the liquid inflames with a match, when the temperature is noted. In many of the states the flashing point is fixed at $44°$ ($111°$ F.); in some as high as $65\frac{1}{2}°$ ($150°$ F.).

297 There has been much speculation as to how petroleum has been produced in nature. Mendeléeff has suggested that it is by the action of water penetrating from the surface and coming in contact with metallic carbides at great depth. This is rendered probable by the fact that carbides are made artificially at very high temperature, and that some of them react with water, yielding hydrocarbons.

5g. *Coal*

298 When wood and similar plant substances decay without free access of air, chemical changes take place by which methane and carbon dioxide are separated, and at the same time the residue contains a larger proportion of carbon. This is somewhat similar in effect to the change produced more rapidly in the charring by heat. The process of decay is seen going on in the accumulations of vegetable matter in swamps and at the bottom of shallow pools as already suggested in another connection; also in the vegetable mold of leaves close to the surface of the ground in the woods. In some places this material has accumulated so that it can be removed like a thick turf, and it is used **299** as a poor kind of fuel, known as *peat* or *turf*. By some such process as this, lasting through ages and modified by heat and pressure, it is supposed that the accumulated vegetation of a period before the appearance of man on the earth, when plant growth was more abundant than now, has been converted into beds of coal. These have become very valuable as a store of fuel, and hence of energy, and very essential to the life and activities of the present. *Lignite* is a variety of coal which still shows traces of the woody structure, and hence is of the more recent formation. *Bituminous* or soft coal has lost the plant

structure, but still contains much hydrogen, and hence yields volatile matter by heating, and burns with a flame. From such coal illuminating gas is made by distillation. *Anthracite* is harder, denser, shows more luster, and burns with little or no flame. Its content of carbon is higher, and it must be the oldest in order of formation. Some varieties seem to have passed almost into graphite. The following table of percentage composition shows the gradual accumulation of carbon through these periods of transformation:

300

	C	H	
Wood	50	6.0	
Peat	60	5.9	
Lignite	70	5.0	
Bituminous	88	5.6	
Anthracite	94	3.4	
Charcoal	96	0.6	Made at white heat (1,500°).
Charcoal	75	4.4	Made at 340°.

5h. *Coal Gas*

301   The important industry of making illuminating gas from coal originated with a Scotchman, William Murdoch. In 1798 a factory was lighted by his process. Gas was used for street lighting in London in 1812, and in Paris about 1815. The process of manufacture in brief consists of heating bituminous coal to a high temperature in retorts of iron or fire clay. The gas is cooled and passed through water, by which tar is deposited and the ammonia which comes from the nitrogen of the coal is removed. This constitutes the chief commercial source of ammonia. From the remaining gas such impurities as hydrogen sulphide, carbon disulphide, and carbon dioxide are removed by the agency of slaked lime or iron hydroxide. The general composition of purified gas is shown in the following percentages (Sadtler):

302

Hydrogen	37.97
Methane	39.37
Carbon monoxide	3.97
Olefins and other heavy hydrocarbons	4.29
Nitrogen	9.99
Oxygen	0.61
Carbon dioxide	0.41

The solid residue of the retorts is coke. From the coal tar, substances of great variety are obtained—such as benzene and its homologues, carbolic acid, naphthalene, pitch, and many others.

DANIEL RUTHERFORD

B. Edinburgh, 1749.   D. 1819.

(See Nos. 306, 388.)

5i. *Destructive Distillation of Wood*

Closely analogous to the distillation of coal is that of wood, which **303** has come to be a considerable industry. The primitive and crude method of charring wood in pits and mounds was for the charcoal only. Improved methods have produced valuable material from the gaseous and liquid portions formerly wasted. Heated below 150°, wood loses water only—from 20 to 50 per cent, according to the variety. From 150° to 280° the dry wood loses about 64 per cent of its weight in volatile products; from 280° to 350° it loses about 6.5 per cent; from 350° to 430°, about 10 per cent; from 430° to 1,500°, only about 2 per cent; so that the yield of charcoal varies from 18 to 20 per cent. From the distillate between 150° and 280° are obtained pyroligneous **304** acid or wood vinegar (a crude acetic acid); wood naphtha, or wood alcohol, which is impure methyl alcohol, CH_4O, a substance homologous with common alcohol, C_2H_6O, and very similar to it; and wood creosote. The distillate between 280° and 350° is mostly gaseous hydrocarbons, and that from 350° to 430° liquid and solid hydrocarbons. The yield of charcoal is greater from slow heating than from quick; it is sometimes more than 30 per cent of the dried wood. Besides the charcoal, the chief commercial products obtained after various purifica- **305** tions are acetic acid and acetates—e. g., of iron, calcium, and sodium, which have uses especially in the dyeing industries; methyl alcohol, or wood spirit, used as a solvent in making varnishes, etc., and in making aniline dyestuffs; acetone, used especially as a solvent; and creosote, used as an antiseptic or preservative. (Sadtler.)

6. NITROGEN

N.—13.93

History.—Rutherford and Priestley in 1772 had under investigation **306** what was later recognized as nitrogen, but Lavoisier was the first to show the elementary nature of the substance and its true relation to the atmosphere. He also named it *azote*, and it still goes by this name in French literature. The name nitrogen comes from *nitrum* or *niter*, the common name for potassium nitrate.

Natural occurrence.—Nitrogen exists uncombined in the **307** atmosphere, of which it forms about four fifths in volume. It is a constituent of nitric acid and its salts, also of ammonia and its salts, and of many organic substances. In-

deed, it plays an important part in the life of both plant and animal, and is an essential element in their food.

308 **Preparation.**—The common source of nitrogen is air, from which the oxygen may be removed by some strongly combustible substance like phosphorus, or even by red-hot copper; and copper shavings moistened with ammonium hydroxide absorb oxygen at ordinary temperature. Other methods of preparing are interesting simply as chemical reactions. Thus, by heating a concentrated solution of ammonium nitrite, the reaction expressed by the following equation takes place:

$$(1)\ NH_4NO_2 = 2N + 2H_2O.$$
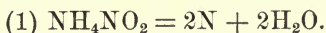
Also, by removing the hydrogen from ammonia, nitrogen is liberated:

$$(2)\ NH_3 + 3Cl = N + 3HCl.$$
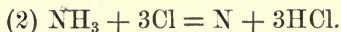
309 **Properties.**—Nitrogen is a gas without·colór or odor, of specific gravity a little less than that of air. One hundred volumes of water dissolve only one and a half of the gas at ordinary temperature. It is condensable to a liquid which is lighter than water and which boils at − 194° and solidifies at −214°.

310 It has no action on litmus, is neither combustible nor a supporter of combustion, is not poisonous, but is incapable of sustaining life. Its chemical inertia is its most striking characteristic, as under ordinary circumstances it reacts with nothing; yet its compounds are numerous and varied, and among the most interesting. At red heat it combines directly with boron, magnesium, silicon, titanium, and vanadium, forming stable compounds. Under the influence of electric discharge nitrogen combines with oxygen, also with hydrogen, so that nitric acid and ammonia are formed in small quantities during thunderstorms and are washed down in the rain. In the presence of alkali carbonate it combines with red-hot carbon, forming cyanogen, C_2N_2. Under silent

electric discharge it combines with some organic substances like cellulose (filter paper), glucose (a kind of sugar), and benzene.

In combination with oxygen it forms a series of five **311** oxides, a most remarkable instance of multiple proportions. The names and formulas of the oxides are as follows:

(1) N_2O, nitrogen monoxide, or nitrous oxide.

(2) NO, nitrogen dioxide, or nitric oxide.

(3) N_2O_3, nitrogen trioxide, or nitrous anhydride.

(4) N_2O_4, nitrogen tetroxide.

(5) N_2O_5, nitrogen pentoxide, or nitric anhydride.

Of these, the first, third, and fifth are acid-forming oxides; the second and fourth are neutral oxides.

6a. *Nitrogen Monoxide, N_2O*

This gas was discovered by Priestley in 1776. It is not **312** found as a natural substance. It is formed to some extent by the action of nitric acid on metals, particularly at a low temperature and when the acid is dilute; but it is best made by heating the dry salt, ammonium nitrate, when the reaction expressed by the following equation takes place:

$$NH_4NO_3 = N_2O + 2H_2O.$$

This reaction is exothermic, liberating 31,000 calories.

Nitrogen monoxide is a gas without color, but with a **313** slight odor and taste. One hundred volumes of water at ordinary temperature dissolve about seventy volumes of the gas. Its specific gravity is about one and a half times that of air—i. e., 21.99 ($H = 1$). It is condensable to a liquid, which boils at about $-90°$ and freezes at about $-100°$. The gas has no action on litmus, although when **314** combined with water it forms *hyponitrous* acid, which, however, is very unstable. The freezing-point method (see Nos. 111 and 155) indicates the formula

$$H_2O.N_2O, \text{ or } H_2N_2O_2.$$
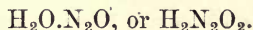
The sodium, potassium, and silver hyponitrites are known, and have the formulas, respectively, $Na_2N_2O_2$, $K_2N_2O_2$, and $Ag_2N_2O_2$. The gas is composed of two volumes of nitrogen and one of oxygen in two volumes of the oxide. Its heat of formation is negative, $-18,000$ calories. This accounts for the fact that the gas supports combustion if the combustible is already ignited and if it produces enough heat to decompose the nitrous oxide. Thus a candle, burning brightly, and sulphur thoroughly ignited, and phosphorus continue to burn in the gas, but they may be extinguished if not already burning vigorously. It is also notable that if they burn, they burn more brightly than in air. The cause of this may be the fact that nitrous oxide, when decomposed, yields a mixture which is one third oxygen, whereas the air is only one fifth oxygen. A mixture of nitrous oxide and hydrogen explodes like hydrogen and air, forming water and nitrogen:

$$N_2O + 2H = 2N + H_2O.$$
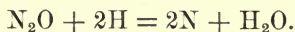
315 While nitrous oxide thus readily gives up its oxygen, it does not easily combine with oxygen as does nitric oxide. It is interesting to note that if nitrous oxide combined directly with oxygen to form nitric oxide, thus,

$$N_2O + O = 2NO,$$
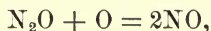
the reaction would involve the formation of four volumes of the product from $(2 + 1)$ volumes of the factors, that is, expansion of volume which would be extraordinary. Furthermore, the reaction would be accompanied by the absorption of about 25,000 calories of heat energy. On the other hand, the oxidation of nitric oxide liberates heat, thus:

$$2NO + 2O = N_2O_4 + \text{about } 40,000 \text{ calories.}$$
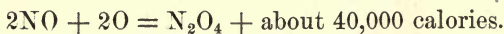
316 Nitrous oxide when inhaled pure produces insensibility, which ultimately ends in death by suffocation, but which passes off if the supply of oxygen be quickly restored to the lungs. It is used extensively as an anæsthetic when insen-

sibility for a short period is desired. If inhaled with air it produces a kind of intoxication, which led to the name " laughing-gas."

6b. *Nitrogen Dioxide, NO*

Nitrogen dioxide, or *nitric oxide*, is not found as a natu- **317** ral substance. It is prepared by removing oxygen from a higher oxide, the pentoxide, which is contained in nitric acid. This is most conveniently done by the agency of metallic copper or ferrous sulphate. When copper is used, the acid should be somewhat dilute (sp. gr. 1.18); small quantities of other nitrogen oxides may be formed at the same time.

The following equations may serve to explain the complex nature of the reaction :

(1) $2HNO_3 = H_2N_2O_6 = N_2O_5 \cdot H_2O.$
(2) $N_2O_5 = 2NO + 3O.$
(3) $3O + 3Cu = 3CuO.$
(4) $3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O.$
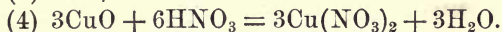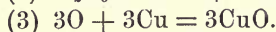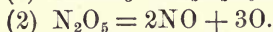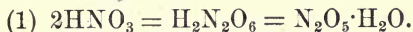
The whole may be expressed in one equation, thus :

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$
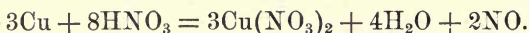
With ferrous sulphate, the reaction is similar so far as the nitrogenous substances are concerned, but by the oxygen which the nitric acid loses, the iron oxide of the salt is changed from ferrous oxide, FeO, to ferric oxide, Fe_2O_3, and consequently the ferrous salt becomes ferric salt. (See Nos. 47/4 and 48, Part II.)

Nitric oxide is a colorless gas, and when pure has no **318** action on litmus. Its specific gravity is 14.95 (H = 1). One hundred volumes of water dissolve about five of the gas at ordinary temperature, but it does not combine with water and has no acid-forming property. It is condensable to a colorless liquid which boils at $-154°$ and solidifies at $-167°$. Like nitrous oxide, it is endothermic with a for-

mation heat of $-21,600$ calories, but it is apparently more stable than the former, and burning sulphur and wood are extinguished by it. Phosphorus and some metals, strongly heated, take oxygen from it. The vapor of carbon disulphide, which also is highly endothermic, burns in it with intense brilliancy. On the other hand, it combines directly with oxygen on contact at ordinary temperature, forming the tetroxide. It dissolves in a solution of ferrous sulphate, combining with the latter, but the product is very unstable. It combines with chlorine at red heat (Ramsay). The gas itself may be exploded by the shock of another explosion, such as that of the fulminate in a common percussion cap (Berthelot).

6c. *Nitrogen Trioxide*, N_2O_3

319   This substance is very unstable, and probably does not exist in gaseous condition, but, when vaporized, becomes a mixture of nitric oxide and the tetroxide; thus:

$$N_2O_3 = NO + NO_2(N_2O_4).$$
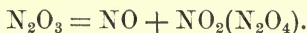
But when the mixture of these gases, or of nitric oxide and oxygen $(2NO + O)$, is cooled, a dark-blue liquid is produced which is supposed to be the trioxide. This, even below $0°$, gives off the brown gas which is a mixture of the two oxides. If this mixture is passed into a solution of basic hydroxide, a salt is formed which is evidently the salt of the trioxide; thus:

$$NO + NO_2 + Na_2O.H_2O = H_2O + Na_2O.N_2O_3 \text{ or } 2NaNO_2.$$
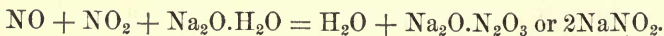
320 This is called *nitrite*, and corresponds to the acid, HNO_2. But when sulphuric acid is added to the solution of nitrite in order to liberate this *nitrous* acid, the latter immediately breaks up into water and the dioxide and tetroxide. When the liquid trioxide is mixed with ice water it is supposed that some nitrous acid is produced; thus:

$$N_2O_3 + H_2O = H_2N_2O_4 = 2HNO_2.$$
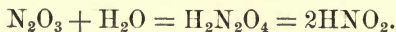
But with a slight rise of temperature this becomes nitric acid and nitric oxide; thus:

$$3N_2O_3 + H_2O = 4NO + N_2O_5 \cdot H_2O, \text{ or } 2HNO_3;$$
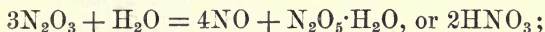
And so, again, a higher and a lower oxide are produced.

Nitrous acid in dilute solution, or its anhydride (N_2O_3), has the curious property of acting both as an oxidizing and as a reducing agent; in oxidizing, it splits into $2NO$ and O; in reducing, it becomes the pentoxide, N_2O_5. Thus it oxidizes the hydrogen of hydriodic acid, HI, liberating the iodine; but it reduces permanganate, destroying its color.

The nitrites are comparatively stable. They are found **321** sometimes in minute quantity in rain water and snow, coming from the atmosphere, and they occur in some plant juices.

6d. *Nitrogen Tetroxide,* N_2O_4

This substance is formed by direct reaction between ni- **322** tric oxide and oxygen or air (compare Exps. $47/_1$ and $47/_2$) at ordinary temperature with evolution of heat, 39,200 calories. It is also formed when some nitrates are heated. Lead nitrate is commonly used. (Compare Exps. $16/_1$ and $16/_2$.)

$$Pb(NO_3)_2 \text{ (dry and heated)} = PbO + O + N_2O_4 \text{ or } 2NO_2.$$
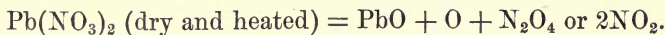
This oxide of nitrogen at sufficiently low temperature **323** is a colorless solid, which melts at $-10°$ to a pale-yellow liquid. This becomes darker as the temperature rises until at $22°$ it boils and the vapor is reddish brown. The color continues to grow deeper until the temperature passes $140°$, when it begins to fade, and at $600°$ or higher the gas is colorless. The specific gravity of the liquid is 1.45 (water $= 1$); that of the vapor just above the boiling point (H $= 1$) is such as to indicate (Gay-Lussac's law; see No. 94) the formula N_2O_4, but at $140°$ it indicates NO_2, and at $600°$ or more the gas is simply a colorless mixture of nitric oxide and

oxygen. When this mixture cools, the gaseous substance NO_2 is first formed, then the gas, N_2O_4, then the liquid, and finally the colorless solid. (Compare with sulphur. See No. 93.) Therefore the solid, the liquid, and the colorless gas, N_2O_4, are to be considered as polymeric (see No. 179) with the dark-colored gas, NO_2. It is convenient to designate the substance NO_2 as the *peroxide* and N_2O_4 as the *tetroxide*. When the peroxide combines with itself heat is liberated; thus:

$$NO_2 + NO_2 = N_2O_4 + 12,900 \text{ calories.}$$
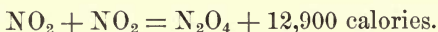
324   The gas has a peculiar odor, and is poisonous. It is an energetic oxidizer and corrosive. Phosphorus may be made to burn in it, and it attacks many organic substances, producing yellow derivatives. It dissolves in concentrated nitric acid, forming the so-called fuming nitric acid of commerce. It forms with water no acid of which it may be regarded as the anhydride, but with ice water it gives both nitrous and nitric acids:

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$

At ordinary temperature and with excess of water the reaction is

$$3N_2O_4 + 2H_2O = 4HNO_3 + 2NO.$$
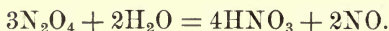
6e. *Nitrogen Pentoxide, N_2O_5*

325   This substance is prepared by removing water from nitric acid, $N_2O_5.H_2O$, by means of phosphorus pentoxide, P_2O_5, and distilling the residue at low temperature. It forms colorless, transparent crystals, which melt at 30° and boil at about 45°. The heat of formation of the solid is 13,100 calories; but that of the gas, curiously enough, is about zero. It is very unstable, breaking up even explosively into the tetroxide and oxygen. It combines with water very energetically, liberating heat and forming nitric acid.

$$N_2O_5 + H_2O = H_2N_2O_6 = 2HNO_3.$$
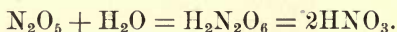
6f. Nitric Acid, HNO_3

This substance was known to the Arabian alchemists, **326** the earliest account of its preparation being that of Geber in the eighth century. He made it by heating a mixture of potassium nitrate, copper sulphate, and alum. Glauber (1603–'68) made it from niter (potassium nitrate) and sulphuric acid, whence its modern name. It has been called " aqua fortis," from its property of attacking metals. Lavoisier in 1776 showed that it contained oxygen, and Cavendish (1784–'85) showed its relation to nitrogen, oxygen, and water.

It occurs in nature free in small quantities, but princi- **327** pally and abundantly in its salts, the nitrates of potassium and sodium.

Nitric acid is formed in small quantity from nitro- **328** gen, oxygen, and water vapor by electric discharge, and is therefore found in the atmosphere. It is also formed as nitrate by the oxidation of ammonia and of the nitrogen of organic substances in the presence of bases. This process is called *nitrification*, and goes on in the soil. It is dependent upon the presence of minute living organisms, called *bacteria*, or at least it is greatly influenced thereby.

Nitric acid is formed, too, when hydrogen is burned in oxygen with a small quantity of nitrogen present, and when ammonia is burned in oxygen.

The chief artificial method of preparation, both on a **329** large and a small scale, is by the action of sulphuric acid on sodium or potassium nitrate, and the distillation of the more volatile nitric acid thus set free. With excess of sulphuric acid, the reaction is as expressed in the equation

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$
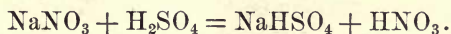
Nitric acid is an important commercial article, and **330** comes into the market as a water solution of specific gravity 1.4, and containing only about 60 per cent, or less, of

the true acid. This is likely to contain as impurities sulphuric acid and hydrochloric acid, or chlorine, and iron salt.

331   When freed of these and of most of the solvent water, it appears as a colorless liquid with a specific gravity of about 1.53, and contains about 99.5 per cent of the true acid, HNO_3. It fumes in the air and absorbs water energetically. It boils at 86° and solidifies at about −50°. When boiled, and even at ordinary temperature, it decomposes to some extent into the tetroxide, oxygen, and water ; as a result of this the liquid, even when more dilute, becomes somewhat yellow and shows the brown fumes. At a higher temperature, 256°, the decomposition is complete. The specific gravity of the vapor slightly above the boiling point is 29.7 ($H = 1$), indicating the formula HNO_3. The substance is very corrosive, attacking many substances violently, and showing a marked tendency to stain organic matter yellow. When the concentrated acid is diluted with water, heat is liberated, and the boiling point of the dilute acid is higher than that of the concentrated, and higher than that of water. If the dilute acid is distilled, it is chiefly water that passes over until the boiling point reaches 121° (normal pressure), when it remains constant, and the distillate contains uniformly about 70 per cent of the true acid. This is supposed to be combined with the water. On the other hand, a solution containing more than 70 per cent of acid, fumes, losing acid, and when distilled the boiling point rises until 121° is reached, when the same constant distillate is obtained. It has already been noted that when dilute nitric acid acts upon metals, reduction products are obtained, as well as the salts.

332   Nitric acid is consumed in large quantities in various industries—for example, in the manufacture of sulphuric acid, of dyestuffs, of nitroglycerine, of guncotton, of the nitrates of silver, lead, and iron ; in the etching of stone, steel, and copper ; in the refining of gold and silver, etc. It is also an important laboratory reagent.

6g. *The Nitrates*

Nitric acid, as shown by its formula, contains one com- **333** bining weight of hydrogen, replaceable by its equivalent of metal. Such an acid is called *monobasic*. It forms a series of well-defined salts, which as a rule are soluble in water. The chief natural nitrates are those of potassium and sodium, which are also important commercial articles. The most abundant is sodium nitrate, which is found in vast beds in portions of Chili and Peru. It goes commercially under the name of Chili *saltpeter*. This has been produced probably by the nitrification of organic matter deposited in what was once the bed of the sea. Before these beds were worked, potassium nitrate, for which there is a large demand, came mainly from somewhat similar deposits in India, particularly in Bengal, where the process of nitrification was artificially cultivated. Now it is made largely by reaction—double exchange—between sodium nitrate and potassium chloride. It is used in making gunpowder and other explosives, and matches; in curing meat, in refining metals, and in medicine. For some of these purposes the sodium nitrate is unsuited by reason of its hygroscopic character, but it is used as a fertilizer, and in the manufacture of nitric acid and potassium nitrate.

6h. *Ammonia, NH_3*

The salts of this substance were known to the early **334** alchemists, especially the carbonate and the chloride. This was called *sal ammoniac*. Priestley in 1774 separated the gas, ammonia. This is formed in the decay of plant and animal substances containing nitrogen, and also when such substances are subjected to dry distillation. It occurs naturally in small quantities in the atmosphere and water, and, as a constituent of its salts, in the soil, and in plant juices and animal fluids. But, as a commercial prod-

uct, it is artificial, its chief source being the gas works. The coal which is distilled contains some nitrogen, about 2 per cent, and this appears as ammonia, a secondary product, in the manufacture of coal gas. It comes into commerce as a water solution which is known as *liquor* or *aqua ammonia*, and contains from 10 to 30 per cent of ammonia gas. A number of its salts are also commercial articles. From its water solution it may be obtained by heating simply, and from its salts by heating with lime, or any non-volatile base.

335   The gas, ammonia, is without color, but has an extremely pungent odor. Its specific gravity is 8.48 (H = 1), and it condenses to a liquid which boils at about −40° and solidifies at about −80°. It can be inhaled only when very much diluted with air, otherwise it is corrosively poisonous. Although its heat of formation is 12,000 calories, it is not formed, save in very minute quantity, by direct combination of nitrogen and hydrogen. When formed, it is relatively very stable. By the passage of electric sparks and by a temperature above 500°, it is slowly decomposed into three volumes of hydrogen and one of nitrogen from two of ammonia. It reacts at ordinary temperature with chlorine in the presence of water, forming hydrochloric acid and pure nitrogen, which is in volume equal to one half that of the ammonia decomposed. It burns in oxygen with a peculiar, pale-yellow flame, forming water, nitrogen, and some traces of nitrogen oxides. In air it burns only with difficulty, the resulting temperature being insufficient to maintain the combustion when it is started. It reacts with many other substances, with acids, and with many salts.

336   In water it dissolves in enormous proportion, one volume of water dissolving about 700 volumes of the gas at ordinary temperature; much heat is thereby liberated, 8,400 calories for 17 grams of ammonia. The gas, however, is readily and completely expelled from the solution by a rise of temperature, and of course an equal quantity

of heat is absorbed in the process. The solution is lighter than water, is alkaline in reaction, caustic, neutralizes acids and forms salts, and reacts in general like the alkali hydroxides—e. g., sodium hydroxide, $NaOH$. From this fact it is supposed that ammonia combines with water *additively*—that is, in such a manner that the product contains *all* the constituents of the factors; and, after analogy with the alkali hydroxides, the product is written NH_4OH, and named *ammonium hydroxide*, although there is little direct evidence of its existence. The name implies a substance, *ammonium*, NH_4, but no such substance has ever been separated. Ammonia combines with acids—e. g., hydrochloric, additively; thus:

$$NH_3 + HCl = NH_3HCl.$$
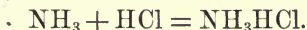
The salt is written NH_4Cl, and named *ammonium* **337** chloride, as if it were formed by displacing the hydrogen of the acid by the substance ammonium, as sodium forms sodium chloride, $NaCl$. When, however, the salt is formed from the hydroxide and the acid, the equation stands,

$$NH_4OH + HCl = NH_4Cl + H_2O.$$
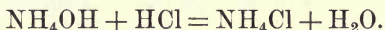
Ammonia, or its solution, is used extensively—e. g., in **338** pharmacy, in calico printing, in manufacturing dyestuffs, soda (i. e., sodium carbonate), and ice. Ammonium sulphate is used in making alum and as a fertilizer, particularly for sugar-beet culture. The chloride, also known as sal ammoniac, is used in pharmacy, in soldering, in galvanizing iron, and in dyeing. The carbonate also is used in dyeing.

6i. *Other Compounds of Nitrogen*

Besides the reactions already described, ammonia takes part in **339** changes of a different type which result in substituting other constituents for its hydrogen. When ammonium chloride in strong water solution is acted upon by chlorine, *nitrogen chloride* is produced:

$$NH_4Cl + 6Cl = NCl_3 + 4HCl.$$

·10

A similar reaction probably takes place with bromine and iodine, producing NBr_3 and NI_3. These substances are extremely explosive, among the most violent known, and consequently very dangerous to handle. Dulong discovered the nitrogen chloride (1811), and lost an eye and three fingers in preparing it, and later Faraday and Sir Humphry Davy were injured by its explosion.

340   Similarly by reaction between ammonia gas and heated metal, compounds are produced in which the metal appears to be substituted for the hydrogen of the ammonia. Thus with sodium are obtained the compounds NaH_2N and Na_3N. These with water yield sodium hydroxide, $NaOH$, and ammonia, NH_3. Some metals form *nitrides* by direct combination with nitrogen—e. g., magnesium, which forms Mg_3N_2, and the latter yields ammonia by contact with water.

341   **Hydrazine** is a second compound of nitrogen and hydrogen. It has the formula N_2H_4, and is a gas of pungent odor. It is very hygroscopic, forming with water a stable compound, $N_2H_4H_2O$. The latter is a very corrosive liquid, which acts as a base in forming salts—e. g., N_2H_4HCl.

342   **Hydroxylamine**, NH_2OH, in water solution acts also as a base, and, like ammonia and hydrazine, combines with acids additively—e. g., $NH_2OH·HCl$.

343   **Hydrazoic acid.***—Most remarkable is this compound of nitrogen and hydrogen, HN_3, which acts as an acid. It is a clear liquid (boiling point, 37°), very explosive, soluble in water, and of intolerable odor. The sodium salt, NaN_3, is soluble, and the silver salt, AgN_3, is insoluble, and both are explosive. A singular reaction is with ammonia, thus:

$$NH_3 + HN_3 = NH_4N_3.$$
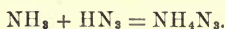
One hydride of nitrogen, acting as a base, combines with another hydride of nitrogen which acts as an acid, forming a salt whose composition is N_4H_4, or, reduced to simplest terms, NH. This, too, is explosive.

With hydrazine also this acid combines additively, giving the salt $N_2H_4HN_3$, or N_5H_5, and this is extremely explosive.

6j. *The Relation of Nitrogen to Living Things*

344   It has already been stated that this element is an essential constituent of the plant and animal organism. Indeed, it is one of the elements in that fundamental form of living matter called *protoplasm* (see No. 191). It seems very probable that the extreme instability or change-

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* Curtius, 1891.

fulness of those substances which are most intimately associated with vital activities is due in large measure to the characteristics imparted by the constituent nitrogen. It is also an element in the rejected waste products of the animal. Therefore its supply must be renewed, and it becomes an essential constituent of food.

345 The higher animals, including man, although they live in an atmosphere which is four fifths free nitrogen and are constantly drawing this into the lungs, are wholly unable to use any of this nitrogen as food. They can not even use nitrates nor ammonium salts as a source of this element. They must have it already as a constituent with carbon and other elements in the organic foods. Such compounds are found particularly in meat, in fish, and in portions of those foods which come from plant seeds, such as wheat and other grains. The higher animals are therefore ultimately dependent on the plant for nitrogenous food, and it becomes of special interest to learn whence the plant obtains its supply of nitrogen.

346 In contrast with the animal, the plant takes its nitrogenous food in the form of ammonia and of nitrates which it finds in the soil. These substances come into the soil in limited quantities, derived from the decay of nitrogenous organic matter which finds its way there. This produces, first, ammonia, and then nitrate, by nitrification, the process being itself dependent on bacterial life (see No. 328). They may also come to some extent from the atmosphere, washed down by rain. But a soil may lose its fertility through exhaustion of its nitrogenous food by the removal of crops; therefore this is restored artificially by the use of fertilizers, such as manures and crude ammonium salts and nitrates.

347 There has been much investigation as to whether the nitrifying bacteria of the soil are able to draw and do draw upon the atmosphere for their supply of nitrogen as they do for oxygen. The evidence seems to show that they do, and that in this manner atmospheric nitrogen ultimately reaches the plant as food. Combined nitrogen, therefore, is valuable, being one of the most costly of food constituents. This has led to many attempts to manufacture nitrogenous compounds cheaply from the nitrogen of the air, but so far they have not been commercially successful.

348 The relation of combined nitrogen in the soil to the food supply of wheat-consuming peoples has attracted much attention. Sir William Crookes* has reckoned that should all the land available for growing wheat be in use, and the present average rate of production be main-

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* Address as President of the British Association for the Advancement of Science, 1898. Chemical News, September 9, 1898.

tained, the total wheat produced would suffice to supply food to the naturally increasing population of bread-eaters, at the present rate of consumption, only until the year 1931. Furthermore, he estimates that the present acreage could meet this increased demand made by increase of population if the average yield of wheat per acre could be raised from the present quantity, 12.7 bushels, to 20 bushels. From results obtained on the experimental farm at Rothamstead, he calculates that this could be done by the use as fertilizer of about twelve million tons annually of sodium nitrate distributed over the world. But the present output of this substance is only about one and a quarter million tons. He then considers the possibility of producing nitrate by electricity—that is, causing the nitrogen and oxygen of the air to combine by electric discharge. From experiments by Lord Rayleigh, he calculates that one ton of sodium nitrate would cost $130, made by electricity from steam power, but only $25 if from water power, as at Niagara.

349   In the same connection he calls attention to the enormous quantity of combined nitrogen which is thrown away in the sewage and refuse of towns and cities, estimating its value for the United Kingdom alone, if it could be recovered, as $80,000,000 per year.

7. OXYGEN

O.—15.88

350   *History.*—Oxygen was discovered August 1, 1774, by Priestley, who made it by heating mercuric oxide, HgO. It was also discovered independently by Scheele, a Swede, at nearly the same time. As early as 1675 Mayow, an Englishman, partly anticipated these more definite discoveries by recognizing some of the peculiarities of air, now known to be due to oxygen. Lavoisier named the gas *oxygen*, signifying the acid-producer.

351   **Natural occurrence.**—Of the elements of the earth, oxygen is the most abundant and the most generally distributed. Uncombined it makes up more than one fifth of the atmosphere, while combined it constitutes eight ninths of all water and about one half, it is estimated, of the earth's crust, including compounds with almost all the other elements.

352   **Preparation.**—It is not practicable to remove the nitrogen from air and thus obtain the oxygen ; other and less
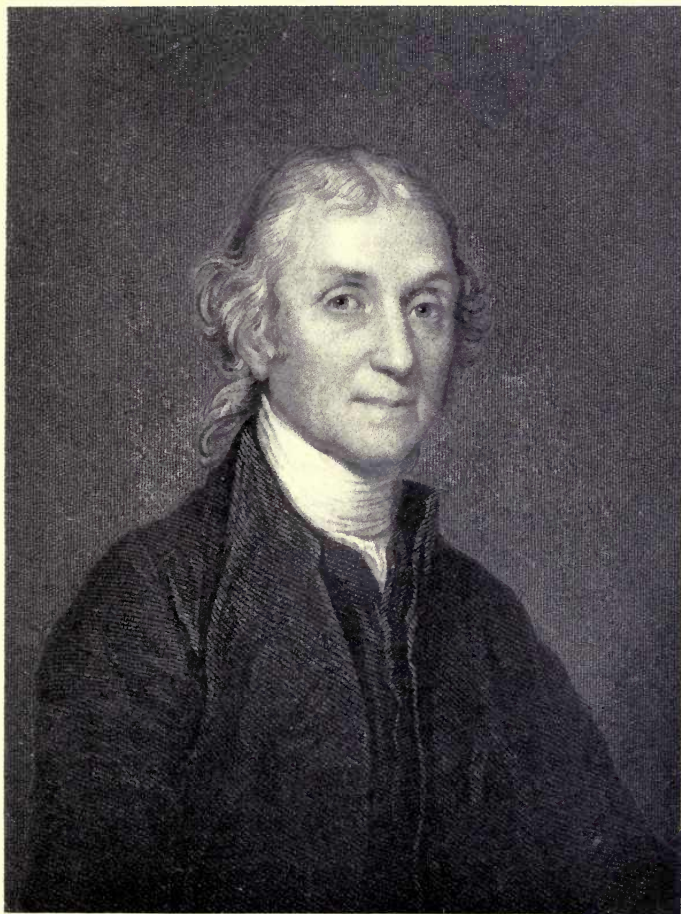
JOSEPH PRIESTLEY
B. England, 1733. D. Pennsylvania, 1804.
(See Nos. 306, 350, 388.)

direct methods are used. It is made (1) by the electrolysis of acidulated water (see No. 202); (2) by heating some metallic oxides—e. g., mercuric oxide and manganese dioxide; (3) by heating potassium chlorate, $KClO_3$, or, preferably, a mixture of this salt with manganese dioxide, which evolves oxygen at a lower temperature than either when alone. Potassium chloride, KCl, is the other product of this reaction. This is the most common laboratory method, and it is also applied commercially for the preparation of oxygen. (4) Another method, which is applied on a large scale in England, consists in heating barium dioxide, BaO_2, under reduced pressure. Oxygen is thus liberated, and the monoxide, BaO, is left. This in turn is heated with air under increased pressure, and the dioxide is reproduced. The oxygen, therefore, comes from air, and the barium oxide serves as carrier.

Oxygen comes into commerce stored under pressure in metallic cylinders.

Properties.—The gas is without color, odor, or taste, and **353** is heavier than air in the ratio of 15.9 to 14.4. Under the pressure of fifty atmospheres and at $-118°$ it condenses to a liquid which boils at $-183°$ (Dewar), and at a still lower temperature solidifies. One hundred volumes of water dissolve 3.1 volumes of the pure gas at 20° and 760 millimeters, but only 0.6 of a volume from the air, since the latter is only one fifth oxygen.

Oxygen is a very reactive substance; binary compounds **354** of it are known with all the other elements except fluorine, bromine, argon, and helium. With most of these it combines directly, with some at ordinary temperature, and with some only at high temperature. The phenomenon of combustion has already been described in other connections, and oxygen has been called a supporter of combustion. But the term is purely relative. Oxygen and air may be burned in an atmosphere of combustible gas, and thus the relative positions be reversed.

355   The *oxides* are of three kinds: those which are acid-forming, those which are base-forming, and those which are neutral—that is, which act neither as base nor acid.   There are some which act as bases in some compounds and as acids in others—e. g., zinc oxide, ZnO, and aluminium oxide, Al_2O_3.   Carbon monoxide is neutral, and many illustrations have already been given of the acid and basic oxides.

356   Oxygen not only supports combustion, but it is necessary to life, at least in the higher forms.   In the animal it is absorbed from the air by the blood and carried to the different parts of the organism, where it effects the oxidation of various substances, and so supplies heat and energy to the system.   When breathed for a short time pure—that is, undiluted by nitrogen—it acts as a tonic, but if breathed longer it becomes harmful, producing fever and weakness; and if inhaled pure and under increased pressure, it acts as a poison.   It is of great service in some diseases, when the ordinary air is not rich enough in oxygen to serve its purpose; also to sustain life in diving-bells and submarine vessels, and in balloon ascensions to the higher atmosphere

357 which is too rarefied to support human life.   It is also used in the oxyhydrogen flame for high temperatures, which finds application in the calcium light.   Its use is found advantageous in the purification of coal gas, in the bleaching of paper pulp, in the thickening of oils for varnishes, etc.   It has been attempted, and with some success, to supply a high-grade illuminating gas by mixing from 15 to 30 per cent of oxygen with the hydrocarbon gas which is made by destructive distillation (T. E. Thorpe).

7a. *Ozone*, O_3

358   When electric sparks pass through air, or through pure oxygen, or, still better, when the passage is by what is called the silent discharge, the gas is found to have a peculiar odor and to be capable of oxidizing mercury and other sub-

stances which are not thus acted upon by oxygen at ordinary temperature. The substance to which these properties are due is named *ozone* (signifying smell). Contraction of volume accompanies its formation, and by bringing this about in pure oxygen and measuring the contraction, then removing the ozone by absorption with turpentine or similar substance, and measuring the second contraction thus produced, it has been found that the latter is twice the former contraction. Therefore, three volumes of oxygen are converted into two of ozone, and the two volumes of ozone are converted into three of oxygen simply by heating. Ozone, then, contains nothing but oxygen—indeed, it is an *allotropic* form of the latter. From the foregoing **360** facts its specific gravity should be $(3 \times 16) \div 2 = 24$. Of the oxygen used, not more than 20 per cent can be converted into ozone, hence it has never been obtained pure; but an approximate confirmation of the calculated specific gravity has been deduced from its rate of diffusion (see No. $203/_1$, Part I), which is nearly the same as that of carbon dioxide (sp. gr. 22).

The formation of ozone accompanies the oxidation of **361** various substances—e. g., moist phosphorus and certain resins, also the burning of hydrogen in air; hence it is generally present in the atmosphere, but only in small quantity—at most one volume in about 700,000. It is more abundant in the air of the country and the seashore than of the city; more during spring than during summer or winter; more during rainy than during clear weather, and it is increased by thunderstorms (Ramsay).

Properties.—Ozonized oxygen seen through considerable **362** depth (one meter with 10 per cent of ozone) is blue, and, when cooled by liquid oxygen to $-180°$, the ozone is condensed to a dark-blue liquid which boils * at $-119°$. In water it is nearly fifteen times more soluble than oxygen,

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* Troost, Comptes Rendus, June, 1898.

according to at least one investigator, but the statements on this point are contradictory.* Its formation from oxygen involves the absorption of 30,000 calories. When it is heated to 250° or 300° it is converted entirely into oxygen with liberation of heat. If heated quickly, especially if under pressure, it explodes. Contact with some substances —e. g., copper oxide—converts it into the original quantity of oxygen without other change. In accordance with its

363 endothermic formation, it is very reactive, acting upon many substances as a powerful oxidizer at ordinary temperature. Some substances—e. g., turpentine—take up the whole of its oxygen; others—e. g., metallic mercury and silver—combine with only one third of its oxygen, liberating two thirds as ordinary oxygen gas:

$$2Ag \text{ (silver)} + O_3 = Ag_2O + O_2.$$
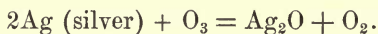
Of similar nature is the reaction with potassium iodide:

$$2KI + O_3 + H_2O = K_2O \cdot H_2O + I_2 + O_2.$$
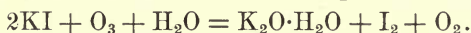
This property is used in order to recognize the presence of ozone, for litmus paper wet with potassium iodide solution turns blue on exposure to ozone, because of the alkali hydroxide formed, or, if starch is present, the liberated iodine turns the starch blue. Curiously enough, ozone may also act as a reducing agent on substances which yield oxygen readily. Thus:

$$PbO_2 + O_3 = PbO + 2O_2.$$
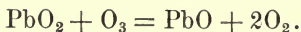
364 Ozone is irritating to inhale in considerable quantity, and fatally poisonous when concentrated. It seems to act as a reducer in the lungs, since the blood appears as it does when suffocation has taken place (Ramsay); still, it is somewhat used medicinally.

365 NOTE.—Ozone may be regarded as an oxide of oxygen or as an elementary polymer. In terms of the atomic theory, its molecule is said to contain three atoms, while that of ordinary oxygen gas contains two atoms of oxygen.

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* Mailfert, Comptes Rendus, 119 (1894).

7b. *Hydrogen Dioxide or Peroxide, H_2O_2*

A substance greatly resembling ozone, so much so that **366**
they can not always be distinguished, is hydrogen dioxide,
H_2O_2. It is said to be formed in small quantity by reac-
tion between water and the oxygen which the former holds
in solution and hence to be present in natural waters. The
chief method of formation—the one used in making the
commercial article—is by the action of dilute sulphuric
acid on barium dioxide :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
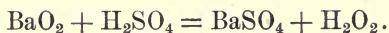
The barium sulphate, being insoluble, is removed by
filtration or decantation, and the dilute solution is concen-
trated by evaporation at low temperature. A solution is **367**
obtained which has the specific gravity of 1.45 and remains
liquid at $-30°$. It has a pungent odor and metallic taste,
and is very unstable. The concentrated solution begins to
decompose at about $20°$, and if rapidly heated may explode.
Under low pressure the dioxide volatilizes at about $84°$,
and a distillate 99 per cent pure is obtainable (Wolffenstein,
1894). The dilute solution is more stable, but by heating
it is entirely decomposed into water and oxygen. This
decomposition is exothermic, liberating 23,000 calories.
Like ozone, it is an active oxidizer, and may also act as a
reducer. It is used in the laboratory as a reagent, in the
arts for its bleaching property, and in medicine as a disin-
fectant and germicide.

7c. *Water, H_2O*

Cavendish in 1781 was the first to show that water, and **368**
water alone, is formed by the combustion of hydrogen and
oxygen. Sir Humphry Davy in the early years of the cen-
tury separated water by electrolysis into hydrogen and
oxygen solely. Gay-Lussac and Humboldt determined its
volumetric composition in 1805, and Berzelius and Dulong

its composition by weight in 1820. Since then, and even in recent years, as stated in another connection (see Nos. 146 and 147, Part I), many have investigated its exact composition.

369   Water is the most abundant compound on the earth. Its presence on the planets Mars and Venus is thought probable. Besides the water which is visible as such is that water which is a constituent of other things but easily separable from them ; for example, water of crystallization. In this sense water is a constituent of many minerals and of both the plant and the animal organism. In plants it constitutes from 50 to 95 per cent of their weight, and the human body yields by drying about 70 per cent of its weight as water.

Many reactions in which water is a product have been already described in other connections, and they do not call for further consideration.

370   **Properties.**—Water is colorless, save when seen through a considerable depth, and it then shows a bluish-green tint. This is seen also in ice and water vapor. When pure, it is without taste or odor. It freezes at 0° and boils at 100° under a pressure of 760 millimeters. Increase of pressure lowers the freezing point and raises the boiling point. It shows its greatest density at 4°, when by definition 1 cubic centimeter of it weighs 1 gram. The specific gravity of ice at 0° is about 0.9—that is, water expands on freezing. In the fusion of 1 gram of ice at 0° to water at 0°, 80 calories of heat are absorbed. In converting 1 gram of water at 100° into vapor at the same temperature 537 calories are absorbed. Water expands more than any other substance in vaporizing, 1 volume of the liquid becoming 1,650 of the vapor. It has also the highest heat capacity. It is a poor conductor of heat and electricity. Its formation heat is 68,400 calories.

7d. *Natural Waters*

Pure water is an artificial product, since natural water, coming in **371** contact with the atmosphere and the earth, takes more or less of matter into solution, and ceases to be pure water in the chemical sense of the term. That which comes in contact with the atmosphere only— that is, rain water (including snow and hail)—is consequently the purest. That which passes over the surface of the land and drains into flowing streams, and that which sinks through the ground and comes to the surface again as spring or well water, must be greatly modified by the nature of the matter with which it comes in contact. More or less of the soluble matter thus picked up is carried on to the sea, where it accumulates; so that sea water contains the maximum of dissolved substances. Rain water sometimes shows as much as 50 grams of solids **372** dissolved in 1,000,000 cubic centimeters of water. River waters vary greatly in the quantity of solids dissolved; for example, in 1,000,000 cubic centimeters of water the river Neva contains only 55 grams of solids; the Seine, from 190 to 432; the Thames—in its upper parts 387, at London from 400 to 450, and in its lower parts 1,617; the St. Lawrence, 170; the Nile, 1,580; the Jordan, 1,052. Spring waters also vary greatly. If solids, especially salts, are present in such quantity as to give marked taste and sometimes odor to the water, it is called *mineral*, and may be used medicinally, even if not acceptable for ordinary drinking. For the latter purpose hardly more than 400 or 500 parts per million would be tolerated, while some mineral waters contain as much as 20,000 or even 30,000. Sea water on the average contains of solids about 36,000 parts per million.

As to the nature of the impurities.—The impurities of rain water are **373** chiefly ammonium salts, nitrates, sodium chloride and sodium sulphate, dust, and germs, besides the normal gases of the air. Of river water, perhaps the most abundant mineral impurities are calcium carbonate and sulphate.

Mineral waters may be distinguished according to their content as **374** follows:

Carbonated waters, containing carbon dioxide, sometimes so much of it that they effervesce, have acid taste, and action on litmus.

Alkaline waters, containing much sodium carbonate.

Bitter waters, containing especially magnesium salts.

Chalybeate waters, containing iron acid carbonate.

Silicious waters, containing alkaline silicates or silicic acid.

Sulphur waters, containing hydrogen sulphide.

Of sea water, sodium chloride (common salt) is by far the most

abundant impurity, showing 25,000 parts or more per million. Next in abundance are magnesium chloride and sulphate, calcium sulphate, and potassium chloride: many other substances are present in minute quantity.

375 **Hardness.**—Waters are called *hard* if they cause precipitation or turbidity when soap solution is added to them, and *soft* in the absence of this property. The soap can not have its desired cleansing effect until the precipitation ceases and the soap remains in solution. Hardness, therefore, since it causes a waste of soap, is in this respect objectionable. The explanation of the precipitation is as follows: Soap is a

375/1 soluble alkaline salt, the base of which is sodium hydroxide (in hard soap) or potassium hydroxide (in soft soap), and the acids of which are the so-called *fatty acids*, which are derived from fats and oils and of which *stearic* acid may be taken as representative. The salts of these acids, with other than the alkaline bases, are insoluble in water. Consequently, when soap solution is added to water which contains *non-alkaline* salts, a precipitate appears which is the non-alkaline salts of

375/2 the fatty acids. The phenomenon of hardness is due, therefore, to the presence in the water of non-alkaline salts. These are commonly salts of calcium and magnesium. If these are present as acid carbonates, they are precipitated by boiling, and the cause of hardness is thereby

375/3 removed. (See No. 271, Part I.) Hardness which is due to non-alkaline acid carbonates is called *temporary*. On the other hand, if it is due to non-alkaline salts other than carbonates, it is not removable by boiling, and is called *permanent*.

376 The nature of the impurities in water has important bearing also upon its suitability for *industrial uses*, such as brewing, bleaching, dyeing, and the processes involved in making textile fabrics; in paper-making; in tanning; in sugar refining. For use in steam boilers, substances like magnesium chloride and free acids, which cause corrosion of the iron, are objectionable; also those which cause deposits or incrustations in the boilers, such as calcium and magnesium acid carbonates and calcium sulphate.

377 The suitability of a water for *drinking purposes* is dependent not only on its freedom from excessive impurities of the kind already indicated, which may be and generally are present in small quantity in good drinking water, but also on the absence of impurities of quite a different order—namely, those which are of plant or animal origin and organic in nature—that is, those which contain carbon, and often nitrogen, and which are subject to putrefaction or decay; and still further on the absence of those minute living organisms called *bacteria*. Natural waters generally contain more or less of the latter, or of their germs,

which are capable of developing and greatly multiplying in favorable conditions. Many kinds of bacteria are quite harmless, but, on the other hand, some greatly dreaded diseases, notably cholera and typhoid, are undoubtedly produced by germs, and very often are transmitted by the drinking water. The presence, therefore, of disease-producing **377/1** germs has come to be recognized as a possible danger in a water supply. Accompanying the excrement of the diseased body, they find their way into the soil and into the sewage, and thence often into the drinking water itself. Evidence, therefore, of the presence in water of substances which are not likely to be there except they come with sewage, even if the substances themselves are entirely harmless, is evidence **377/2** of possible danger, since the germs themselves may at any time be present in the water if once they reach the sewage. In addition to this, it is probable that even water contaminated with organic matter of plant origin or with the sewage of healthy persons may cause diseases such as diarrhœa, to say nothing of the disgusting possibility of drinking dilute sewage, even though it be without harm.

One substance which almost always accompanies refuse matter of animal origin is sodium chloride (common salt). It is also present nor- **377/3** mally in most waters, and in any quantity which is acceptable to the taste is entirely harmless. If, however, it is found present in excess of what may be regarded as normal in a given sample, it is reckoned as giving a valuable indication of probable pollution by sewage. The same may be said of ammonia and of nitrates and nitrites. Ammonia is **377/4** produced by the decomposition of nitrogenous organic matter, whether by the slow process of decay or by the quicker processes of chemical reaction ; the nitrates and nitrites are also the last products in the oxidation of such matter. The presence, therefore, of these substances beyond their normal quantity for a given sample of water gives warning of probable contamination. Finally, an approximate measure may **377/5** be got of the number of living germs which water contains by sowing a small measured volume of the sample in a medium suitable for their rapid growth, and, after a sufficient interval, counting the visible growths. Some degree of success has been reached in identifying the specific germs of certain diseases, but the chemical indications just mentioned give information much more readily than those which depend on the actual identification of germs.

7e. *Purification of Water*

Filtration on a small scale is the treatment most commonly **378** employed for the purification of drinking water. This strains out mat-

ter in suspension, and renders turbid water more acceptable in appearance. But clearness is no test at all of purity; a water may be perfectly clear and at the same time most dangerously impure. Many filtering materials are in use, and they differ widely in their effects, although

379 they may all serve to clarify. Charcoal, especially animal charcoal, removes suspended matter, and to some extent organic dissolved matter, and reduces the temporary hardness; but it does not remove bacteria. Indeed, by furnishing a favorable medium for their growth it may actually increase them and itself become a source of danger.

380   Stone, sand, spongy iron, and prepared paper are proposed for domestic filters, but none of them affords any protection against the danger from harmful bacteria. Porous earthenware or unglazed porcelain may strain out the bacteria almost completely, but it loses its efficiency with use. Filters of this kind are generally supplied in the form of cones or cylinders, through which water is forced by hydrant pressure or simply by atmospheric pressure. These should be removed at least once a week, cleaned, and heated for thirty minutes in boiling water or in an oven (Mason).

381   *Distillation* affords the most perfect purification of water, but it is not so easily available for domestic use, although largely used at sea.

382   *Boiling* for fifteen or, better, thirty minutes, by killing the bacterial life, affords most useful protection against danger, "and should be invariably resorted to in case of waters which bear any suspicion of sewage contamination. The vapid taste of the boiled water may be removed by passage through a filter, which, however, should be exclusively employed for this purpose and not for filtering unboiled water" (Frankland).

383   *The purification of drinking water on a large scale* for city supplies is undertaken in some places with good results. By the use of large settling basins and of extensive filtering beds suitably constructed of gravel and sand, the public water supply may be greatly improved. Such filtration properly conducted is found to remove bacteria almost completely. This surprising result is due to the growth upon the sand of a kind of slime which acts as a filtering membrane, and the sand is not effective until this formation has taken place. Besides straining out the bacteria, this filtration tends to nitrify the organic matter and thus to improve still further the condition of the

384 water (Mason). In some places a small quantity of alum is added to water which contains acid carbonates. A slight precipitate of the gelatinous aluminium hydroxide is thus produced, which takes the place of the slime above referred to, and permits the more rapid filtra-

tion through coarse sand with the same desired result. At the same time no appreciable quantity of alum goes into the filtered water. There can be no reasonable doubt that the treatment of drinking **385** water on the large or on the small scale as herein described is capable of furnishing, as proved by results, a valuable, although of course not complete, protection to public health against certain diseases.

The purification of water on a large scale for *industrial purposes* **386** is also undertaken, particularly the removal of temporary hardness and of those substances which cause boiler deposits. The common method is precipitation, followed by filtration or subsidence. As precipitating material, various substances are used, such as calcium hydroxide (lime-water), sodium hydroxide, sodium carbonate, sodium fluoride, and sodium aluminate.

7f. *Action of Water on Lead and Zinc*

As lead pipes are very commonly used to convey drinking water, **387** and as lead compounds are poisonous and tend to accumulate in the body, it becomes an important sanitary matter to know whether lead may be carried into the water by contact with the pipes. That some varieties of natural waters do corrode the lead, and that many instances of poisoning have been thus caused, is not to be doubted. That other varieties do not attack the lead is also true. Hard waters, especially those containing acid carbonates, do not, as a rule, take up lead; nor do all waters without acid carbonates act upon it, but many certainly do so act. The fact with regard to a given sample is best ascertained by direct experiment. So small a quantity of lead as 0.7 parts per million of water is reckoned as unwholesome for continued use (Frankland).

Zinc also is acted upon by many waters, but the quantity taken up is small, and its presence is not regarded as serious. Copper should not be used in contact with drinking water, for it is easily corroded and is poisonous. Tin is the least acted on of the available metals.

B. The Atmosphere

The atmosphere is the gaseous envelope which surrounds the earth. **388** In the ancient Greek philosophy of Aristotle, air, earth, water, and fire were the four elementary principles out of which were made all substances. Boyle in the seventeenth century was one of the first to investigate scientifically the nature of air; but the discovery of nitrogen by Rutherford in 1772, and of oxygen by Priestley in 1774, alone made

possible the explanation of the true nature of air which was put forth by Lavoisier in 1777. The quantitive relation between the oxygen and nitrogen was established in 1781 by Cavendish.
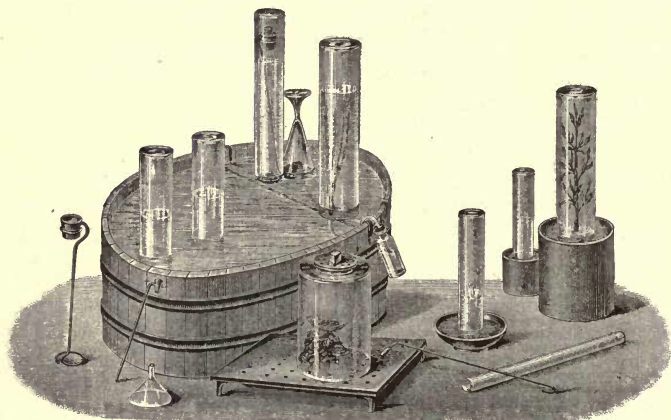
FIG. 4.—Priestley's apparatus for the investigation of air and other gases.

389   Various estimates have been made of the distance above the earth to which the atmosphere extends. From observations of twilight its height has been calculated as about fifty miles. With this height it bears the relation to the earth that a film one twelfth of an inch in thickness bears to a globe one foot in diameter (Roscoe). Its weight is such as to make a pressure which is variable, but which averages 1033.3 grams per square centimeter at the sea's level (about 15 pounds to the square inch). This is equal

390   FIG. 5.—Lavoisier's apparatus for examining air by heating a volume inclosed in a retort and in contact with mercury.

to the weight of a column of mercury 1 square centimeter in section and 760 millimeters high (= 29.9 inches).

The atmosphere is a mixture in which the nitrogen and **391** oxygen so greatly exceed the other substances in quantity that it is customary to speak of air as made up of these two gases. But besides these there are present argon, water, carbon dioxide, nitric acid, ammonia, ozone, hydrogen (according to Gautier, C. R., November, 1898, 1.5 parts in 10,000), hydrogen dioxide, complex organic substances, and dust, including the germs of living organisms. All of these may be easily removed except the nitrogen, oxygen, and argon; and, considering the mixture of these three for the moment as *air*, it may be stated that one liter of it **392** weighs 1.293 grams at 0° and 760 millimeters, which is 14.40 times the weight of the same volume of hydrogen. In such free air the ratio of nitrogen (including argon) to oxygen is remarkably constant, as found by analysis of samples collected over land and over sea, at widely separated points of the globe, on the tops of mountains, and at the greatest height reached by balloons. The greatest variation is only about 1 part in 200. The nitrogen (including argon) averages 79.04 and the oxygen 20.96 per cent by volume, or by weight 77 and 23 per cent respectively. Nevertheless, in some exceptional instances of free air and in the air of confined spaces, such as buildings and mines, the oxygen has been found to vary beyond the limit first mentioned, falling as low as 20.26 per cent in mines. It has been thought by some that at extreme heights the **393** air may be slightly richer in nitrogen owing to the slight difference in the specific gravity of the two gases, but this does not seem to be established by evidence. A sample of air collected at the height of 15,500 meters (51,000 feet) by means of an " aërophile " in February, 1897, gave 20.79 per cent of oxygen by volume and 79.21 per cent of nitrogen, including argon (Cailletet).*

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* Comptes Rendus, March 8, 1897.

394   **Air a mixture.**—That the nitrogen and oxygen are free and not combined in air is proved by the following facts:

(1) Their relative quantity is subject to slight but unmistakable variation.

(2) The density of air is equal to the mean density of the two gases, reckoned in their respective quantities.

(3) Each substance dissolves in water according to its own degree of solubility, and, since oxygen is considerably more soluble than nitrogen, air which is dissolved in water is richer in oxygen than is undissolved air, the proportion of oxygen by volume being increased from 21 to 35 per cent. It is upon this dissolved oxygen that fishes and other gill-breathing animals depend.

(4) By drawing air through a rubber membrane, the proportion of oxygen may be increased to 42 per cent (Graham).

(5) Nitrogen and oxygen may be mixed in their due proportions without evolution of heat or change of volume, and the mixture shows all the properties of air.

(6) Air may be liquefied, and even frozen, and, when the temperature of the mixture is allowed to rise slowly, the nitrogen, having the lower boiling point ($-194°$), volatilizes first, and soon the liquid becomes nearly pure oxygen —boiling point $-183°$.

395   **Liquefaction of air.**—Air was liquefied in 1883, but only in small quantity. Quite recently the process has been operated on a very much larger scale and more cheaply, so that it has been proposed to make liquid air a commercial article, and to apply it to a great variety of purposes. In Dewar's method of liquefaction the gas is put under pressure of 120 to 140 atmospheres, and passed through coils of copper pipe which are inclosed in a vessel whose walls are protected against the passage of heat by layers of non-conducting material. The coils are cooled to $-80°$ by solid carbon dioxide. The gas thus brought to this low temperature is allowed to escape through a small hole, and its sudden expansion still further reduces the temperature of the escaping gas which is conducted over the coils. By this means the gas con-

tained in the latter is reduced to lower and lower temperatures, until it liquefies and drops into a receiving vessel. This is protected against access of heat by a double wall, the space between the two walls being vacuous.

C. Argon

The next constituent of the atmosphere following nitrogen and **396** oxygen in quantity is *argon*. It was not discovered until 1894, having been previously reckoned and identified with the nitrogen, although Cavendish, in his investigation of the ratio of nitrogen to oxygen, suggested the possibility that something other than nitrogen was present in small quantity. In an elaborate investigation of the density of gases, Lord Rayleigh determined with great accuracy the weights of equal volumes of nitrogen obtained from air by removal of the oxygen, and of nitrogen obtained by five different chemical reactions, with the following results:

Nitrogen by chemical decomposition.		Nitrogen from air.
2.3001 grams.		2.3103
2.2990	"	2.3100
2.2987	"	2.3102
2.2985	"	Mean, 2.3102
2.2987	"	
Mean, 2.2990	"	

The means showed a difference considerably larger than any probable error of determination, and this led him to suspect the presence of a heavier gas with the atmospheric nitrogen. Associated with Professor Ramsay he passed the nitrogen from air over hot magnesium, which takes up nitrogen. and thus obtained a small quantity of gas which would not combine with magnesium nor with oxygen by the electric spark. This was the new element which they named *argon* (signifying inactive). It has since been found occluded by several minerals and a meteorite and dissolved in some mineral waters. It is present in air to the extent of 1 volume in 100, and therefore the percentage of true nitrogen must be reduced to 78. (Argon = 0.94 % of air, Schloesing.)

The gas condenses to a liquid which boils at −187°, and solidifies to **397** white crystals which melt at −190°. One hundred volumes of water dissolve about four of the gas, which gives it about the same solubility as oxygen. Its specific gravity is 19.81 (Ramsay, December, 1898). All of the many attempts to make it enter into combination have failed; its chemical properties other than this are therefore unknown,

According to Gay-Lussac's law its combining weight should be 19.81, but certain physical properties which it possesses are thought by some to indicate 39.62 as the proper value.

Other New Elements in the Atmosphere

398   Ramsay has stated that he has succeeded in separating other gaseous substances from air, which, at the present stage of investigation, appear to be elements hitherto unknown. They may suitably be mentioned in connection with argon and air, although their general properties have not been sufficiently determined to permit of full description, nor indeed has their existence been established beyond doubt.

Neon (signifying new) is the name given to one of these. It was obtained by liquefying 18 liters of atmospheric argon by means of liquid air, and subjecting the liquid to fractional distillation. Separating the more volatile portion and redistilling it, Ramsay finally (1898) obtained a gas having a specific gravity of about 9.5 ($H = 1$) and more volatile than nitrogen and argon, and differing from them also in other properties. He estimates its quantity as 1 volume in 40,000 volumes of air. Like argon, it shows certain physical properties which lead some to the conclusion that 19.0 rather than 9.5 should be reckoned as its combining weight (Chemical News, September 23, 1898).

399   The same investigator thinks he has evidence of three additional gases in the less volatile portions of the liquid, which consisted in the main of argon, all coming from the atmosphere. These he has named *krypton* (signifying hidden), *metargon*, and *xenon* (signifying the stranger). They are present in still less quantity than the neon. To metargon he gives a specific gravity about the same as that of argon. The evidence seems not yet sufficient to establish the existence and elementary nature of these three substances (December, 1898).

400   *Helium* is the name given to a substance which, on the evidence of the spectroscope, was supposed to be present in the sun. After the discovery of argon in 1894, Ramsay found this substance—i. e., argon —present in a gas which is obtained from certain minerals and which had previously been regarded as nitrogen. In so doing he found (March, 1895) still another gas, the spectrum of which was identified with that of helium. The presence of the latter substance on the earth had not before been noted. Then, in December, 1898 (see Chemical News, January 27, 1899), he found helium with neon in the crude argon from air. It has also been found in a number of minerals and mineral waters, and, like argon, in a meteorite. Its specific gravity ($H = 1$) is 1.98 (Ramsay, January, 1898). As in the case of argon, no attempts to make it enter into combination have succeeded. It shows the same

physical property which is possessed by argon, neon, and metargon, and this fact leads some to think that its combining weight also should be taken as twice the specific gravity.

Its boiling point is about the same as that of liquid hydrogen (Dewar, 1898), and it dissolves in water to the extent of 7 volumes in 1,000.

8. FLUORINE

F.—18.91

Natural occurrence.—Fluorine was first isolated in 1886 **401** by Moissan. It is found in nature only in combination. Its compound with calcium, CaF_2, is known as *fluorite* or *fluor spar*, and is quite abundant. *Cryolite*, $AlF_3(NaF)_3$, is brought in large quantities from Greenland. Combined fluorine also occurs minutely in bone, blood, the enamel of teeth, and in sea and mineral water.

Preparation.—Moissan obtained it by electrolyzing in a **402** tube made of platinum and iridium, and at a low temperature ($-23°$), pure anhydrous hydrogen fluoride, HF, mixed with potassium fluoride, KF.

Properties.—It is described as a greenish-yellow gas of **403** a peculiar odor, probably due to the formation of ozone when fluorine comes in contact with moisture. It condenses at the temperature of boiling liquid air to a clear yellow liquid, which boils at $-187°$, does not solidify at $-210°$, has a density of 1.14 (water $= 1$), and is soluble in all proportions in liquid air and oxygen.

The gas at ordinary temperature combines with hydro- **404** gen explosively, and attacks substances which contain hydrogen, forming hydrogen fluoride or hydrofluoric acid, HF. From water it liberates oxygen as ozone. Indeed, it combines with nearly all the elements, and at lower temperature and with more energy than does oxygen. It is the most reactive substance known, and its properties make it extremely dangerous. With oxygen no compound has been obtained. Reduced in temperature to $-190°$, it does

not react with carbon, water, mercury, glass, nor some other substances; but it still reacts, accompanied by incandescence, with hydrogen and with hydrocarbons like turpentine. In the course of the experiments which gave these remarkable results some drops of liquid fluorine fell upon the floor, instantly setting the wood on fire (Moissan and Dewar, November, 1897).

405   *Hydrofluoric acid* is made by the action of sulphuric acid on a fluoride—e. g., calcium fluoride, CaF_2:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
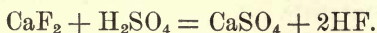
406   It is a colorless, fuming liquid, boiling at 19°. The density of the gas, slightly above 19°, indicates the formula H_2F_2, but at 100° it indicates HF. It is one of the most corrosive substances known. As a gas it is intensely poisonous to inhale, and in contact with the skin it produces most painful sores. Those dealing with it protect themselves with rubber gloves and apron. It dissolves most of the metals, forming salts—the fluorides—and it dissolves also the substance of rocks, like sand and granite, which is a silicate. It also attacks glass, which is an artificial silicate, forming with the silicon a gaseous silicon fluoride, SiF_4, hence its use in etching. It is very soluble in water, and its solution comes into commerce stored in bottles of rubber or of ceresine (a natural paraffin).

9. SODIUM

Na.—22.88

407   *History.*—The element, sodium, was separated from caustic soda, its hydroxide, by Davy in 1807. It was a remarkable discovery, as the caustic soda had been regarded as elementary.

408   **Natural occurrence.**—The element is not found free, but occurs abundantly, chiefly in the chloride, common salt. This is found in sea water, constituting about three per cent of the same; also in mineral waters, and in extensive

SIR HUMPHRY DAVY
B. England, 1778.   D. 1829.
(See Nos. 220, 235, 407, 442, 527, 533, 549, 577.)

beds of "rock salt" in the earth's crust. The nitrate, carbonate, sulphate, silicate, and other salts of sodium are found native, and it is sometimes a constituent of plant and animal organisms.

Preparation.—The element was originally separated by **409** Davy from its hydroxide by electrolysis. Later its manufacture was greatly cheapened by a process which consists of heating to a high temperature—a white heat, in iron cylinders—a mixture of sodium carbonate, coal or charcoal, and chalk (calcium carbonate). The reaction is thus expressed:

$$Na_2CO_3 + 2C = Na_2 + 3CO.$$
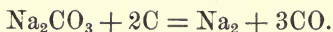
The liberated sodium is separated by distillation. This method was improved in 1886 by Castner, who used sodium hydroxide and a mixture of iron and pitch (giving, perhaps, a carbide of iron). By heating, is brought about this reaction:

$$6NaOH + 2C = 2Na + 6H + 2Na_2CO_3;$$
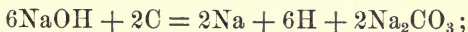
and the sodium is distilled as in the first process. Still later, since the cheapening of electricity, the older process of electrolyzing the fused hydroxide is coming into use.

Properties.—Sodium is a soft, white, crystallizable metal **410** of silverlike luster. Its specific gravity (solid) is 0.98, and it melts at 96° and boils at 742°. In dry air it remains untarnished, but in moist air it oxidizes, and when heated it burns with a brilliant yellow flame, forming both the monoxide, Na_2O, and the dioxide, Na_2O_2. It combines directly with fluorine, chlorine, bromine, and iodine. It decomposes water at ordinary temperature, liberating hydrogen and forming the hydroxide, $NaOH$, a base. For these reasons it is kept under kerosene or some similar liquid. By heating in hydrogen, a hydride is formed, Na_2H (?). Sodium combines with carbon, forming the carbide Na_2C_2, which with water yields acetylene, and it forms with nitrogen the nitride Na_3N, which with water

yields ammonia.   The dioxide does not form salts, but it readily yields one half its oxygen, and is used somewhat as an oxidizing agent.

Sodium has a considerable industrial use in obtaining other metals like magnesium and aluminium from their chlorides and in processes involving the removal of oxygen (reduction).

9a. *Sodium Chloride, NaCl*

411   It has been already stated that this substance is formed by direct action between the elements and by the action of hydrochloric acid on the metal and on its oxide and hydroxide.   But it is the most abundant of all the compounds of sodium, and therefore is the available natural source for those manufactured compounds which are in commercial demand.   It some parts of the world it is mined and brought to the surface like other rock.   In other places it is obtained by the evaporation of strong solutions or brine. In warm countries even sea water is evaporated by exposure to the sun and wind in order to obtain the salt which it contains, and in some cold countries repeated freezing is resorted to, since removal of the ice, which is relatively free of salt, tends to concentrate the solution.   Salt is produced in one way or another in many places, and the aggregate is enormous.   Perhaps the best known salt regions in this country are those of central New York and of Michigan.

412   Sodium sulphate, calcium sulphate, and magnesium chloride often accompany common salt as impurities, and the last substance causes it to be deliquescent.   Pure sodium chloride does not show this property unless in air saturated with moisture.   It crystallizes in cubes without water of crystallization, melts at 851° (V. Meyer), and volatilizes at a slightly higher temperature.   One hundred grams of water dissolve 36 grams of salt at 0°, and 40 grams at 100°.

9b. *Sodium Carbonate*, Na_2CO_3

This substance is found in nature, but not in sufficient **413** quantity to meet the commercial demand, and its manufacture constitutes one of the most important of chemical industries. It is known also as soda, soda-ash, sal-soda, and washing soda. Until 1793 its commercial source was the ashes of sea plants. At the time of the revolution France was cut off from her supply of this important article, and the Government called upon chemists and manufacturers to make public their processes for making it from common salt. The method invented by Leblanc proved the most successful, and is still in use without essential modification. The English manufacture, which has since become very extensive, was started in 1823 under the Leblanc process.

The Leblanc process.—This, although somewhat compli- **414** cated in the practical details, is simple in the fundamental reactions which are involved. It consists of three stages :

(1) *The " salt-cake " process.*—This consists in making sodium sulphate from the chloride by the action of sulphuric acid. The first reaction is

$$2NaCl + H_2SO_4 = HCl + NaHSO_4 + NaCl.$$

When the temperature is further raised, the second reaction takes place :

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$
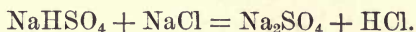
The hydrochloric acid is condensed in water and thus becomes a by-product in the manufacture. The salt cake consists of sodium sulphate to the extent of 96 or 97 per cent. A considerable quantity is used in making glass.

(2) *The " black-ash " process.*—Salt cake, 100 parts, limestone or chalk, 100 parts, and coal, 50 parts, are mixed and heated in a furnace to about 1,000° under suitable conditions. The reaction which takes place is in the main as follows :

(a) $Na_2SO_4 + 2C = Na_2S + 2CO_2$.
(b) $Na_2S + CaCO_3 = Na_2CO_3 + CaS$.
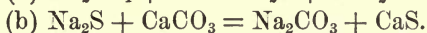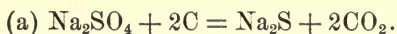
The black ash appears as a brownish-black porous material, and contains from 37 to 45 per cent of sodium carbonate, about 30 per cent of calcium sulphide, CaS, and from 5 to 10 per cent of calcium oxide, CaO, and many other substances in smaller quantity.

(3) *Treatment with water.*—The purpose of this is to dissolve the carbonate and leave the sulphide, but undesirable reaction between the substances is likely to occur, especially if too much water is used or if the temperature rises above 60°. The solution thus obtained is submitted to various purifications, is further concentrated, and finally deposits crystals of crude carbonate. These, dried and ignited, are " soda-ash," and by re-solution, purification, and crystallization yield the " soda crystals," $Na_2CO_3.10H_2O$, still somewhat impure.

415 **The Solvay ammonia process.**—Since 1872 large quantities of sodium carbonate have been made by this rival process. It consists of saturating brine (i. e., a solution of sodium chloride) with ammonia, cooling the solution, and then passing in carbon dioxide. The reaction is

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

The acid carbonate, being less soluble than the ammonium chloride, is separated by precipitation. The reaction is not complete, about one third of the sodium chloride being lost.

From the acid carbonate is obtained the normal carbonate by heat alone:

$$2NaHCO_3 \text{ (heated)} = Na_2CO_3 + CO_2 + H_2O.$$
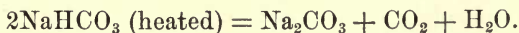
The carbon dioxide thus recovered is used over again. From the ammonium chloride the ammonia is also recovered with some loss:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$
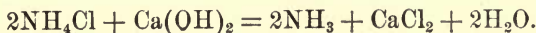
By this process is produced a soda-ash of 98 or 99 per cent purity.

These two are the chief commercial methods of produc- **416** ing sodium carbonate, which is consumed in great quantities, finding use in the making of glass, of soap, of caustic soda, and for many other industrial and domestic purposes.

The dry salt is hygroscopic but not deliquescent, melts **417** at red heat, and at higher temperature volatilizes. Its solution has alkaline reaction.

Sodium acid carbonate, $NaHCO_3$, known also as bicar- **418** bonate of soda and as baking soda, loses carbon dioxide and water at a comparatively low temperature, and for this reason is used as a constituent of baking powder.

9c. *Sodium Hydroxide, Caustic Soda, NaOH*

This substance is made from the carbonate or from the **419** crude material at a certain stage of the Leblanc process by removing the carbon dioxide through the action of lime, $Ca(OH)_2$. A dilute solution of the crude carbonate is brought to boiling temperature, and lime is added with constant stirring. Calcium carbonate is formed, and, with the other insoluble material, is allowed to settle, and the liquid, after various purifications, is concentrated in iron pots by boiling until the temperature reaches about 260°, when the mass becomes very stiff and contains nearly 64 per cent of sodium oxide, Na_2O. At this stage air is blown in or nitrate is added, in order to oxidize the remaining sulphide. The mass is kept in a fused state for eight or twelve hours, by which impurities of iron, aluminium, and silicon oxides settle to the bottom. The clear liquid is then ladled off into iron drums or other suitable vessels, in which it solidifies on cooling. In this form it appears in commerce. It is also produced in granular condition. (Compare No. 546.) The commercial article may contain as much as 95 or 96 per cent of the hydroxide, and as

impurities some carbonate, sulphate, chloride, silicate, and aluminate. It is used extensively in soap-making, paper-making, bleaching, in the manufacture of dyestuffs and of wood pulp, in refining oil, and in many other operations. (Lunge, in Thorpe's Dictionary of Applied Chemistry.)

420 The purer material for chemical purposes often appears cast in sticks. It is a white crystalline solid which absorbs water and carbon dioxide from the air. It melts and volatilizes. It is very soluble in water (about 2 parts to 1 of water), dissolving with evolution of heat. A crystallized hydrate, $2NaOH \cdot 7H_2O$, is obtainable, which dissolves with absorption of heat. The hydroxide is a powerful base, and its solution is much used in the laboratory.

421 Of the other salts of sodium, the sulphate occurs naturally, and its manufacture has already been described. It is known sometimes as Glauber's salt. The nitrate, known as Chili saltpeter, is found abundantly, and is valuable as a source of nitric acid. It is also converted into potassium nitrate, which is used extensively in making gunpowder. The borate—i. e., borax—has been referred to in connection with boric acid.

D. General Survey

422 Nine elements have now been considered descriptively, and there will be gain in taking a general view of their properties for the purpose of comparison, first with reference to some physical properties. *As to condition at ordinary temperature*, it is to be noted that the first one is gaseous; then follow four which are solid; the next three are gaseous, and the ninth is solid. Closer examination as to this matter, by comparison of melting or boiling points (see Table VI, No. 433), shows that among the solids the melting point tends to rise with increasing combining weight for the four—lithium, glucinum, boron, and carbon; and then to drop to a low value for the next one—namely, sodium.

As to combining volume—that is, the volume in cubic **423** centimeters occupied by the combining weight measured in grams—it should be recalled that these volumes are approximately equal for the elements in gaseous condition (Law of Gay-Lussac); for solids and liquids the case is different. In column III are given these combining volumes. They are equal to the combining weight divided by the specific gravity of the solid or liquid. It is to be observed that they go decreasingly from lithium through carbon, and then increasingly to sodium.

Comparison as to the chemical relations is next made, **424** and of these, first *as to the fact of combination* with other elements, forming binary compounds—i. e., compounds of two elements only. It is interesting to note that all the elements so far considered exist in binary compounds with hydrogen and with chlorine, and all except fluorine with oxygen. This leads to the question: May each element combine with every other one? Now, the metals, like lithium, glucinum, and sodium, as a general rule, mix with each other in the liquid condition and form what are called *alloys*, but there is more or less doubt whether these **425** should be reckoned as chemical compounds, or as physical mixtures. Furthermore, the existence of borides of lithium, of glucinum, and of sodium seems unproved, although not improbable. With these exceptions, it may be affirmed that each element is known to exist in binary combination with every other one, so far as concerns the first nine.

As to readiness of combination—that is, the readiness **426** to enter directly into combination with other elements— hydrogen combines directly with lithium, but only on heating, and the heating must be continued, or the reaction ceases; similarly with glucinum. Direct union between hydrogen and boron seems not to have been observed. With hydrogen and carbon, the union takes place only under the influence of the electric arc; similarly with nitro-

gen. With hydrogen and oxygen, direct union takes place on elevation of temperature, and the reaction is continuous, while explosive union with fluorine takes place at ordinary and even very low temperatures. With sodium, direct combination is effected as in the case of lithium.

427   *Oxidation* in the case of hydrogen is already considered; with lithium it takes place at slight elevation of temperature; with glucinum, boron, and carbon at higher temperature; with nitrogen only under strong electric influence; similarly with oxygen (formation of ozone); with fluorine not at all; and with sodium about the same **428** as with lithium. Indeed, with the exception of sodium, it would seem that the elements so far considered enter into combination with each other the more readily as they are further removed from each other in the list.

429   *As to energy of combination*, comparison may be made by noting the quantities of heat liberated in combining with oxygen, and also with chlorine. These values, so far as determined, are given in columns VI and VIII. In both instances it is seen that the values tend to increase to a maximum and then decrease, and that the change is very marked in passing from fluorine to sodium.

430   *As to capacity of combination:* By comparing the formulas of the chlorine compounds in order (column VII), it is seen that the coefficient of the chlorine symbol, beginning with one, increases to four for carbon, then decreases to one for sodium. The capacity of combination thus illustrated is named *valence*. It is an important phenomenon, and calls for some further consideration (No. 434).

431   *As to base-forming and acid-forming oxides:* For convenience the basic function may be represented by the plus sign and the acidic by the minus sign. The facts are thus tabulated in column V: Lithium oxide acts only as base; the oxide of glucinum acts primarily as base, but in the glucinates as acid; that of boron is primarily acid, but in the compound, BPO_4, seems to act as base; those of car-

bon and nitrogen show no basic function; that of sodium is basic only. The disappearance of the basic function, the appearance of the acidic, and the reappearance of the former with sodium are very remarkable.

It will be recalled that this descriptive work has been **432** introduced under the general topic, " The relation between the properties in general of the elements and their combining weights." But up to this point there has been no suggestion as to the nature of the relation. The clew to this will perhaps be seen in this general survey, but it will not be formulated until later in the course. It is recommended that the student in the meantime bear the question in mind, to see if he can not, by following the clew already given, trace the development of the relation in the continuation of descriptive facts soon to be presented.

TABLE VI   **433**

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Melting points. Boiling points.	Combining volumes.	Oxides.	Base and acid.	Formation heat of oxides.	Chlorides.	Formation heat of chlorides.
					Calories.		Calories.
H...	B. P. $-238°$	(Liquid) 14	H_2O	?	(Liquid) 68,400	HCl	22,000
Li ..	M. P. 180°	11.8	Li_2O	+	141,200	LiCl	93,800
Gl ..	M. P. 1,230°	4.9	GlO	+−	?	$GlCl_2$	?
B ...	(Sublimes) 3,600° ?	4.4	B_2O_3	− +	317,200	BCl_3	104,000
C ...	(Sublimes) 3,600° ?	(Diamond)3.4	CO_2	−	97,000	CCl_4	21,000
N....	B. P. $-194°$	?	N_2O_3	−	−23,000	NCl_3	−38,100
O....	B. P. $-183°$	(Liquid) 14.3	O_3	?	−32,400	OCl_2	−17,800
F ...	B. P. $-187°$	(Liquid) 16.6	?	?	?	?	?
Na..	M. P. 96°	23.2	Na_2O	+	100,400	NaCl	97,600

E. VALENCE

The valence of an element is by definition its capacity **434** of combination, as measured by the multiple of the combining weight of hydrogen which enters into combination with the combining weight of the element in question. It is seen, therefore, in the coefficients of H in the formulas of the hydrides—for example, HF, H_2O, H_3N, and H_4C. Hydrogen being made the unit, it is assumed that the capacity of combination of one gram of this element is the same

in all compounds. The four hydrides just mentioned are gaseous, and their formulas are well established by the law of Gay-Lussac concerning vapor densities; but the hydrides of lithium and glucinum are not gaseous, and the composition of boron hydride is not yet well established. Of many other elements also it is true that they do not form hydrides, or that the composition and vapor density **435** of the same are not determined. However, most such elements do form chlorides, and chlorine and hydrogen must have the same capacity of combination, since their compound has the formula HCl established by quantitative relation both in weight and in volume, and by the specific gravity of the gaseous compound. Chlorine, therefore, may be taken as the measure of valence when hydrogen is not available. The series of chlorides is exhibited in column VII.

436   Better to appreciate the basis of valence, let the argument be recalled which led to the choice of certain multiples of the equivalent weights to be used as combining weights of the elements (see Nos. 136, 137, 150, and 151, Part I). This choice was determined by relations of specific gravity, of specific heat, of depression of freezing point and elevation of boiling temperature in solutions, besides others which were not specified. In addition, it was stated that the choice was greatly strengthened by the relation of the elements as to their properties in general. The force of this relationship may now be seen. Carbon was the element then used for illustration, and the choice for combining weight of the multiple by four of its equivalent weight was in question, since the specific gravity of gaseous carbon is unknown. It is now evident that were any other multiple chosen, the position of carbon in the series of elements would be changed, and the remarkable progression of properties brought out in this general survey would disappear. From this point of view it is seen that the measure of valence is found in the factor by which the

equivalent weight is multiplied to produce the combining weight.

Clearly, then, the valence of elements is best determined **437** in their binary compounds with hydrogen or with chlorine. Those whose combining capacity is equal to that of hydrogen or chlorine are called *monads*, and are said to be *univalent ;* those which have twice the capacity of hydrogen or chlorine are called *diads*, and said to be *bivalent ;* correspondingly, those which have three, four, five, six, and seven times the capacity of hydrogen are named respectively *triads*, *tetrads*, *pentads*, *hexads*, and *heptads*. The adjectives are *trivalent, quadrivalent, quinquivalent, sexivalent,* and *septivalent.*

Statement I.—The valence of a given element may vary **438** in combination with the same substance; for example, in hydrogen dioxide, H_2O_2, the valence of oxygen appears to be one half that of the same element in water, H_2O ; so also the valence either of carbon or of oxygen must vary in the compounds, CO and CO_2 ; and the valence of nitrogen or of oxygen must vary in the compounds, N_2O and NO. Indeed, every instance of multiple proportions must indicate apparent variation in valence.

Statement II.—The valence of a given element may vary **439** according to the substance in combination with it. Thus if oxygen is a diad, then nitrogen in the substance, NO, must act as a diad ; but in ammonia, H_3N, it is certainly a triad ; in ammonium chloride, NH_4Cl, if it be granted that four fifths of the capacity of nitrogen is taken with hydrogen and one fifth with chlorine, the nitrogen must be acting as a pentad.

Statement III.—Valence must influence the phenome- **440** non of substitution as well as that of combination. Thus lithium and sodium are univalent in their chlorides, $LiCl$ and $NaCl$. They must therefore act as monads in the replacement of hydrogen from hydrochloric acid and other acids. This is seen again in the nitrates, $LiNO_3$ and Na-

NO_3, in the carbonates, Li_2CO_3 and Na_2CO_3, and in the acid carbonates, $LiHCO_3$ and $NaHCO_3$. Concerning magnesium and zinc, let it be recalled that 24 grams of one and 65 grams of the other replace 2 grams of hydrogen; they are therefore diads, and their chlorides are $MgCl_2$ and $ZnCl_2$, their nitrates $Mg(NO_3)_2$ and $Zn(NO_3)_2$, and their carbonates $MgCO_3$ and $ZnCO_3$. In other words, the capacity of combination has the same value as the capacity of substitution. (Compare Law IV, Equivalent Proportions.)

441   *Statement IV.*—The valence of a compound is regarded as dependent on the valence of its constituents. If the maximum valence of these is not exhausted, then the compound may add to itself some substance, or *combine additively*, as it is expressed. Thus the capacity of 14 grams of nitrogen is not exhausted in ammonia, NH_3, since the latter combines with hydrochloric acid additively, forming ammonium chloride, NH_4Cl, in which the capacity of nitrogen is exhausted. So also nitric oxide, NO, takes on oxygen and becomes the peroxide, NO_2; and CO becomes by combustion CO_2. The same is seen in compounds of greater complexity, for sodium nitrite, $NaNO_2$, becomes by oxidation the nitrate, $NaNO_3$. Those substances capable of additive reaction, and therefore possessing a residual valence, are called *unsaturated*, the others *saturated*.

441/a   *Statement V.*—The phenomena of oxidation and reduction (see Nos. $47/_4$, 48, and $208/_1$, Part II), in which one substance takes the oxygen that another substance gives up, involve, as is evident, a change in valence. Thus when ferrous oxide, FeO, is changed to ferric oxide, Fe_2O_3, or when ferrous salts are changed to ferric salts by the oxygen which nitric acid yields, the active valence of the iron is increased from two to three and that of the nitrogen is reduced from five to two, for that of the oxygen is reckoned as constant. The terms oxidation and reduction are sometimes applied to similar changes in valence when the element oxygen is not at all involved. Thus the change of

mercuric to mercurous iodide by reaction with added mercury may be spoken of as reduction; and the change of mercurous to mercuric iodide by reaction with added iodine is sometimes designated as oxidation, although this seems an unfortunate extension of meaning.

Review Problems

1. How many grams of hydrogen should be liberated by the action **441/1** of 10 grams of pure sodium on water? What is the volume of this mass at 0° and 760 millimeters (one liter of hydrogen weighs 0.0899 of a gram at 0° and 760 millimeters)?

2. Suppose that 10 grams of pure carbon are burned in oxygen, how much does the product of combustion weigh? What is its volume (one liter = 1.98 grams)? What is the volume of the oxygen contained in it?

3. What is the specific gravity of methane (H = 1)? What is the volume of the combustion products from one liter of methane? What is their total mass?

4. Suppose that one liter of water vapor is passed over hot carbon and completely decomposed, what is the volume of the products taken under the same conditions of temperature and pressure as the water vapor?

5. What is the specific gravity of ammonia gas (H = 1)? Suppose one liter of dry ammonia gas is to be obtained from ammonium chloride, how may it be done, and how much of the latter substance is theoretically needed?

6. What is the ratio between the masses of dry ammonia and pure sodium hydroxide, which in water solution neutralize equal quantities of hydrochloric acid?

7. How much dry sodium carbonate is needed to make 10 grams of sodium nitrate? To make 10 grams of sodium chloride?

8. Assume that one gram of diamond is completely burned, and the product of combustion completely absorbed by sodium hydroxide, how much carbonate is thus produced?

9. Assume that carbon dioxide is liberated from the carbonate thus produced (problem 8) and completely reduced to carbon by hot magnesium, how much magnesium oxide is thus produced?

10. As between 26 grams of acetylene on one hand, and on the other 24 grams of carbon and 2 grams of hydrogen which the former contain, which gives out more heat in burning? (See No. 57, Part I.)

As between methane and acetylene, at the same price per cubic foot, which is the more effective fuel, assuming complete combustion in both

cases? (See No. 57. The formation heat of methane is 21,800 calories.) What is the ratio of efficiency?

11. Assume that "natural gas" is pure methane, that pure calcium carbide is obtainable, that one cubic foot of acetylene weighs 1.17 ounces, and that the cost of water is zero—at what price per pound for the calcium carbide would acetylene be as cheap for fuel as "natural gas" at fifty cents per thousand cubic feet?

10. MAGNESIUM

Mg.—24.10

442   *History.*—Magnesia was distinguished from lime in 1755, but Davy was the first to separate the metallic element.

443   **Natural occurrence.**—It is not found free, but is abundant as a constituent. The mineral *dolomite*, which is very abundant, is the carbonate of magnesium and calcium. *Magnesite* is the carbonate. Asbestos, talc, or soapstone, and meerschaum contain it as a silicate. The sulphate is known as Epsom salt and is found in mineral waters, as is also the chloride. It occurs in small quantity in the plant and animal organism, and the spectroscope shows it present in the sun.

444   **Preparation.**—It is obtained from the fused chloride by electrolysis and by the action of sodium :

$$MgCl_2 + 2Na = Mg + 2NaCl.$$
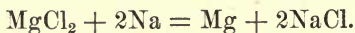
It is purified by distillation in hydrogen or coal gas.

445   **Properties.**—It is a metal of a clear, white color. It is malleable, and when heated it is ductile—that is, it can be hammered or rolled into thin sheets and drawn into wire. Its specific gravity is only 1.75. It melts at red heat, 700° to 800°, and boils at about 1,000°. It does not oxidize in dry air and only superficially in moist air. Heated in air, it burns with an intensely brilliant light, which fact is made use of in signaling, in pyrotechnics, and in photography. The oxide, MgO, is produced in burning, and, if the oxygen be insufficient, considerable nitride, Mg_3N_2,

is also produced by direct union with the nitrogen. It combines when heated with hydrogen (MgH ?),* with boron, carbon (MgC_2), nitrogen, oxygen, fluorine, chlorine ($MgCl_2$), bromine, iodine, silicon, phosphorus, and sulphur. It slowly decomposes boiling water and is quickly acted upon by dilute acids. Its energetic combination with oxygen makes it a powerful reducing agent.

Its sole oxide, MgO, known also as *magnesia*, appears **446** generally as a fine white powder, almost insoluble in water, but soluble by dilute acids with the formation of salts. It melts and crystallizes only at extremely high temperature, but does not decompose; it is therefore the most serviceable material for the construction of electric furnaces and for similar uses. Its boiling point is not far above its melting point (Moissan). With water it forms the *hydroxide*, MgO_2H_2, which is only sufficiently soluble in water to give alkaline reaction with litmus, and which dissolves in acids, but not in potassium or sodium hydroxide.

Of the salts of magnesium the following are the most **447** important commercially : The chloride, $MgCl_2$; carbonate, $MgCO_3$; nitrate, $Mg(NO_3)_2$; and sulphate, $MgSO_4$.

11. ALUMINIUM

Al.—26.9

History.—Alum, a salt of aluminium, was known to the alchemists, **448** Geber and Paracelsus. Much later, in 1754, it was learned that the earthy base of alum, which was named alumina, is unlike that of lime and the same as that of clay. But it was not until 1827 that the element was obtained from its oxide, alumina. Its name, therefore, comes from its salt, alum. (The spelling, aluminum, is in equally good usage.)

Natural occurrence.—It has not been found free; but as **449** a constituent, next to oxygen and silicon, it is the most abundant and most generally distributed of the elements in the earth's crust. The oxide, Al_2O_3, constitutes *corun-*

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* Winkler, Ber. Chem. Ges., 24 (1891).

dum, and when crystallized the ruby (red) and the sapphire (blue). *Bauxite* is the hydrated oxide, $Al_2O_3 \cdot 2H_2O$, with iron oxide. As silicate, alumina is present in very many minerals—e. g., feldspar, granite, garnet, mica, slate, soapstone, and clay. *Cryolite* is a fluoride, $Al_2F_6 \cdot 6NaF$; turquoise, a phosphate. It is found in fertile soils and to some extent is taken up by plants (Berthelot). By the spectroscope its presence in the sun is revealed.

450   **Preparation.**—Wöhler obtained it by reaction between dry aluminium chloride and potassium; Bunsen and Deville in 1854 by the electrolysis of the fused chloride; and Deville about the same time by the action of sodium on the fused double chloride of aluminium and sodium. In consequence mainly of the latter's work it was prepared in quantity promising a commercial supply, and his method remained for thirty years practically the only one in use. Before considering more fully the manufacture of the metal, it is best to study its properties and some of its compounds.

451   **Properties.**—It is a white, lustrous metal with a specific gravity of 2.58 (cast) or 2.7 (hammered), which is remarkably low as compared with that of zinc 7.1, tin 7.3, iron 7.8, copper 8.9, silver 10.5, and lead 11.4. It melts at about 660° (Holman, 1896), and volatilizes only at the extremely high temperature of the electric furnace. In compact condition it gives out a peculiar sound when struck. Like other metals, it is a good conductor of heat and electricity. It may be worked, like gold and silver, into very thin leaf of 0.000638 millimeters (one forty-thousandth of an inch) in thickness, and it may be drawn into very fine wire. It has great tensile strength as compared with other metals, and this and its low specific gravity make a combination of properties very valuable in mechanical applications.

452   Aluminium does not easily combine with oxygen. It tarnishes very slightly in air, and even when melted oxidizes only superficially, but at white heat it burns brilliantly, forming the oxide, Al_2O_3. If in the form of very

FRIEDRICH WÖHLER

B. Germany, 1800.   D. 1882.

(See Nos. 178, 216, 450.)

thin leaf, it burns more readily. In compact form the metal does not appreciably decompose water even at red heat. But this, like the difficulty of direct oxidation, is probably due to the formation of a film of oxide which protects the metal from further action. If this protection is reduced or removed, the reaction goes on. Thus the thin leaf slowly decomposes water at 100,° with the liberation of hydrogen. Likewise, if a soluble salt of aluminium be present in the water, the action goes on, for the protecting film is dissolved by the salt. If the metal is dissolved in mercury, or if the clean surface is simply rubbed with mercury, it decomposes water at ordinary temperature. With **453** hydrochloric acid the pure metal reacts readily, forming the soluble chloride and hydrogen; but with dilute sulphuric acid and with nitric acid the action in ordinary circumstances is inappreciable; but it goes on progressively if the metal is finely divided, or if the pressure of the atmosphere on the surface of the liquid is removed, so that the liberated hydrogen is free to escape from the surface of the metal. It dissolves readily in the presence of sodium chloride and other chlorides with the addition of a little free acid, such as acetic. In solution of sodium or potassium hydroxide it dissolves easily, liberating hydrogen and forming the aluminate in which its oxide acts as acid to the alkali base ($Na_2O \cdot Al_2O_3$, and $K_2O \cdot Al_2O_3$). In ammonium hydroxide the action is slower.

The metal combines directly with fluorine, chlorine, **454** bromine, and iodine, forming Al_2X_6 or AlX_3; also with boron, carbon, (C_3Al_4), nitrogen, (AlN), silicon, and sulphur, (Al_2S_3). A compound with phosphorus, Al_3P_5, has been obtained. [L. Frank and Rossel, Ber. Chem. Ges., 27 (1894).]

The commercial metal.—The presence of impurities changes consid- **455** ably the properties of the metal, both physical and chemical, and therefore the descriptions by different observers vary greatly according to the sample examined. The usual impurities of the commercial metal

are iron, silicon, carbon, nitrogen, and sodium. Their presence probably tends to make the impure metal harder, and of higher melting point, to reduce the tenacity, malleability, and ductility, and to increase the readiness to react chemically.

456 **Alloys.**—This is the name given to the compounds or mixtures of metals with metals. In many cases fused metals may be mixed in all proportions, and in some instances there seems to be real chemical union, as shown by the evolution of heat and the formation of crystallizable compounds of definite composition. Still, the true nature of alloys is not at all well understood.

457 Aluminium forms alloys with readiness, and they have special interest. Although a small percentage of iron in aluminium deteriorates it, on the other hand a small percentage of aluminium in iron and steel is advantageous. Aluminium forms alloys with copper in all proportions. The one containing ten per cent of aluminium is known as "aluminium bronze." It rivals the best steel in tenacity, is very hard, casts well, may be highly polished, and resists corrosion well. These properties adapt it to many useful applications.

458 **The oxide, alumina.**—The single oxide of aluminium has the composition Al_2O_3. Its natural occurrence as corundum, ruby, and sapphire has already been mentioned. Emery is an impure form containing iron. Alumina is made by burning the metal, also by drying the hydroxide. Artificial rubies and sapphires are made by dissolving alumina in fused barium fluoride and allowing it to crystallize. A trace of chromate is added to make the ruby, or of cobalt oxide to make the sapphire. The crystals thus obtained have all the properties of the natural crystals. They are next to the diamond in hardness. The oxide in the amorphous condition is a white powder. It melts and volatilizes in the heat of the electric arc. It is insoluble in water, but dissolves in acids and in sodium and potassium hydroxides. By strong heating its density is increased, and it is less readily acted upon chemically. It acts both as a base-forming and as an acid-forming oxide.

The hydroxide, $Al_2O_3 \cdot 3H_2O$ or $Al_2O_6H_6$.—This appears as **459** a white gelatinous precipitate when a solution of a hydroxide, as that of sodium, or potassium, or barium, is added to a solution of an aluminium salt:

$$Al_2Cl_6 + 6NaOH = \underline{Al_2O_6H_6} + 6NaCl.$$
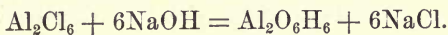
It is insoluble in water, although a peculiar, allotropic form is soluble, but it dissolves in acids, in sodium hydroxide and potassium hydroxide, and in the solution of a normal aluminium salt, in the last case forming a basic salt. It dissolves but slightly in ammonium hydroxide. Besides the tri-hydrate, the di-hydrate, $Al_2O_3 \cdot 2H_2O$, and the mono-hydrate $Al_2O_3 \cdot H_2O$. occur as natural minerals.

Uses.—The hydroxide has a peculiar property of uniting, either **460** chemically or mechanically, with many dyestuffs. If the solution of a dye is added to the solution of an aluminium salt, or of an aluminate, and the hydroxide is then precipitated, it carries in many instances the color stuff into the precipitate. This mixture is called technically a "lake." By means of this property, dyes are "fixed" in textile fibers which otherwise would not retain the color. When the hydroxide is deposited in or upon the fiber and there retains the dye, it is called a "mordant." The aluminium compounds find extensive use as mordants.

Aluminium salts.—The chloride, when anhydrous, is vola- **461** tile without decomposition, and its vapor density at low temperature indicates the formula Al_2Cl_6, and at high temperature $AlCl_3$. It is soluble in water, but can not be recovered from solution by evaporation, as it loses acid and becomes the hydroxide.

The sulphate, $Al_2(SO_4)_3$, is the most common of the salts. With the alkali sulphates, it forms double salts which crystallize readily. They are called the *alums*, com- **461/1** mon alum being $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. The same term has come to be applied to the similar double sulphates with other bases than aluminium—e. g., iron and chromium. Common or potash alum is found as a natural mineral to some extent, and is manufactured in large quantity, being used not only as a mordant, but in the making of leather,

of paper, of fire-proof material, etc. Its manufacture and use as a mordant are of great antiquity.

The salts with silicic acid—i. e., the silicates—occur in great variety as natural minerals. The carbonate and the sulphide are not formed in the presence of water.

11a. *The Manufacture of Aluminium*

462   The properties of this metal which promised to give it wide applicability in the useful arts, if it could be produced cheaply enough, and the abundance of its ores have led to innumerable attempts, more or less successful, to reduce the cost of its production. For about thirty years after its introduction—that is, until about 1885—the process of Deville, at Salindres, France, furnished practically all the aluminium of commerce. In this process the ore used is bauxite, containing about 50 per cent of aluminium oxide, Al_2O_3, and 25 per cent of iron oxide, Fe_2O_3. Four steps are involved in the process:

(1) The formation of sodium aluminate. This is effected by heating the ore with sodium carbonate in a furnace. The reaction is

$$Al_2O_3 + 3Na_2CO_3 = (Na_2O)_3Al_2O_3 + 3CO_2.$$
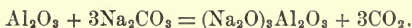
The aluminate by its solubility in water is separated from the iron of the ore, the presence of which is very objectionable.

(2) The production of the oxide free from iron. This is accomplished by saturating the water solution with carbon dioxide, when the following reaction takes place:

$$(Na_2O)_3Al_2O_3 + 3CO_2 = Al_2O_3 + 3Na_2CO_3.$$
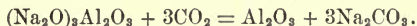
The alumina precipitates, and nearly the whole of the original carbonate is recovered from the filtrate.

(3) The conversion into chloride. The washed and partly dried alumina is mixed with sodium chloride and charcoal, and the mixture is moistened with water and worked into balls. These are completely dried, heated to redness, and treated with chlorine gas. The following reaction takes place:

$$Al_2O_3 + 3C + 6Cl = Al_2Cl_6 + 3CO.$$
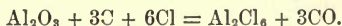
The chloride and the salt form the double chloride $Al_2Cl_6 \cdot 2NaCl$, which, being volatile, distills.

(4) The reduction of the chloride by sodium. The double chloride is mixed with cryolite (to serve as flux) and sodium. The mixture

is quickly introduced into a red-hot furnace, and the reaction takes place with great energy:

$$Al_2Cl_6 + 6Na = 2Al + 6NaCl.$$
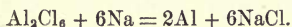
When the reaction is finished and the mass is in quiet fusion, the melted metal separates at the bottom of the furnace and is drawn off and cast as desired.

There were thus produced 1,800 kilograms in 1872, and the selling **463** price was \$20 per kilogram. By 1886 the cost had been reduced one half, and the English industry was competing with the French, but by the improved Deville process. From 1883 to 1888 an industry was developing in Germany which returned to the electrolytic method of Bunsen and Deville, cheapened by the availability of dynamic electricity. The fused chloride, or fluoride, was the material employed.

Two methods of American origin have special interest for their **464** conspicuous success. That of Hall (Pittsburg) was patented in 1889. This improves the earlier electrolytic methods by dissolving alumina in a fused mixture of aluminium salts and others, and electrolyzing only the former without affecting the solvent. He was able to reduce the price in 1889 for aluminium, 98 per cent pure, to \$4.50, and later to \$2 per pound, which in 1887 had been \$8. The Cowles (Cleveland) process was patented in 1885. In this, as in the Heroult Swiss process, which dates from 1888, the aluminium is not produced pure, but in alloy with some other metal such as copper. Alumina and carbon, and the other metal, copper, in coarse mixture, are placed in a rectangular furnace (Cowles process) so arranged that the powerful electric arc from carbon poles strikes through the mass. The great temperature of the arc liquefies the mass, and alumina is reduced, either by the action of the carbon, or by electrolysis, or by both combined, and in fused condition it alloys with the copper and is drawn off at the base of the furnace, carbon monoxide burning at the top. (Thorpe and J. W. Richards.)

In 1896 the world's production of aluminium had increased to **465** 1,789,000 kilograms, and in 1897 to 3,400,000 kilograms, and the price had been reduced to 60 cents per kilogram. (R. Meyer's Jahrbuch.)

12. SILICON

Si.—28.2

History.—Silica, the oxide of silicon, and minerals containing it, **466** were used in remote antiquity for glass-making. It was long considered as an earth like lime, but in 1660 the fact was observed that, unlike such substances, it could not neutralize acids, but acted rather like an

acid, combining with alkalies. Its compound nature was surmised by Lavoisier, but Berzelius in 1810 first obtained the element, although in impure condition. In 1823 he obtained the pure substance.

467 **Natural occurrence.**—The free element has never been found native, but as oxide, SiO_2, it is next to oxygen the most abundant element, constituting, according to estimate, one quarter of the earth's mass. Sand, quartz, agate, flint, and opal are forms of silica, while most rocks, except the carbonates, are mixed silicates. Silica is found also in plants, especially the grasses, and in animals to some extent.

468 **Preparation.**—It is obtainable by reaction between aluminium, or magnesium, and silica in the electric furnace; also by the reducing action of carbon on silica at this high temperature; also by the action of aluminium or of sodium on silicon chloride:

$$3SiCl_4 + 4Al = 3Si + 2Al_2Cl_6.$$
$$SiCl_4 + 4Na = Si + 4NaCl.$$
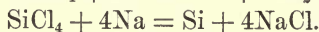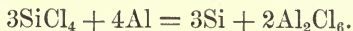
But the processes are difficult, and the element is therefore rare.

469 **Properties.**—It exists in three conditions, the amorphous, the graphitoidal (like graphite), and the crystalline, thus resembling carbon. The amorphous silicon is a dark-brown powder, with the specific gravity of 2.15. It fuses and volatilizes only at extremely high temperature. It is insoluble in water and in acids other than hydrofluoric, and soluble in sodium and potassium hydroxides. With hydrofluoric acid, it forms hydrofluosilicic acid, thus:

$$Si + 6HF = H_2SiF_6 + 4H.$$
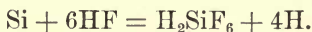
And with alkalies it forms silicates:

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 4H.$$
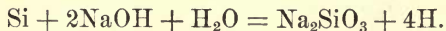
When heated in air, or in oxygen, silicon burns brilliantly, forming the dioxide SiO_2. It combines directly at ordinary temperature with fluorine, forming SiF_4, and with chlorine,

when heated, forming $SiCl_4$. Besides the latter chloride, the following have been obtained: Si_2Cl_6, Si_3Cl_8, Si_2Cl_4. (Compare with the hydrocarbons Nos. 278 and 279.) The hydride, SiH_4, is a gas which under some conditions takes fire on contact with air, burning to water and silicon dioxide, SiO_2. A compound with carbon, SiC, has already been mentioned (No. 258). At least one with nitrogen is known, probably, of the composition Si_2N_3 (?), and one with sulphur, SiS_2. With many of the metals silicon combines directly.

The crystallized silicon is steel-gray in color, hard **470** enough to cut glass, has a specific gravity of 2.5, and is less readily acted upon than is the amorphous.

Silica or silicon dioxide.—This substance is formed by **471** the oxidation of silicon, and by the dehydration of silicic acid. The native silica, quartz, is found often in transparent crystals, very hard, sometimes white and sometimes tinted. It is frequently named rock crystal. Amethyst, agate, onyx, flint, hornstone, jasper, and opal are varieties. It also exists in amorphous condition, both native and artificial, the latter a fine white powder. It may be melted in the oxyhydrogen flame, and in the electric arc it boils and volatilizes. It is insoluble in water, but dissolves in hydrofluoric acid. If the latter is anhydrous, the gas, silicon fluoride, is formed:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$
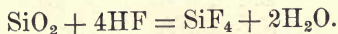
If water is present, the fluoride is decomposed, forming silicic acid and fluosilicic acid, thus:

$$2SiF_4 + 3H_2O = H_2SiO_3 + H_2SiF_6 + 2HF.$$
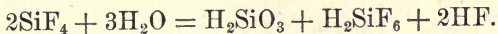
It is by virtue of these reactions that hydrofluoric acid at- **472** tacks glass, which is a mixture of silicates. The amorphous silica dissolves in the alkaline hydroxides, only slightly in that of ammonium, also to some extent in the alkaline carbonates, in both cases forming soluble alkaline

silicates, in which it acts as acid. In one compound—namely, $SiO_2 \cdot P_2O_5 \cdot 4H_2O$—it would seem to act as base to phosphorus pentoxide, which is certainly acid (Haute-feuille).

473   Silicic acid and the silicates.—Silica is an acid-forming oxide, combining with water in varying proportion, and forming a series of silicic acids. The simplest one—and it may be taken as typical of the rest—is $H_2O.SiO_2$, or H_2SiO_3, sometimes designated as metasilicic acid. This is obtained as a white gelatinous precipitate by adding hydrochloric or other acid to a solution of alkaline silicate :

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl.$$

This precipitate is soluble in sodium and potassium hydroxides, and in excess of hydrochloric acid, less so in ammonium hydroxide. By drying and heating, it loses its water, and the anhydrous silica does not dissolve by hydrochloric acid. The silicic acid may also be obtained in a form which is soluble in water, but which is unstable and is thrown into the insoluble form by the presence, even in small quantity, of various substances, the change liberating heat. Whether this is an allotropic form or a different hydrate is

474 not known. Silicon dioxide combines with metallic oxides in great variety of ratio and complexity, forming the almost innumerable silicates which make up the greater part of the earth's crust. The silicates of the alkalies, sodium and potassium, are soluble in water, although in solution they are decomposed by carbonic acid, and even by water itself in dilute solution, for the silicic is a very feeble acid. To keep them in solution, therefore, requires some excess of the alkali base. Silica occurs in some natural waters, either as soluble silicic acid or as alkaline silicate. To the slow deposition of silica from such solution is due probably the formation of silicified or petrified wood and shells, very beautiful samples of which are often found. The non-alkaline silicates are insoluble in water.

The comparison of silicon with carbon is extremely in- **475** teresting ; in its predominating quantity and in the characteristics which it imparts to its compounds, the former seems to bear much the same relation to the mineral world that carbon bears to the world of living things.

12a. *Some Uses of the Silicates*

Soluble glass.—This is sodium or potassium silicate, or a mixture of **476** the two. It is made by fusing 3 parts of silica mixed with 2 parts of potassium carbonate, or with 3 parts of sodium carbonate ; or by heating silica with a solution of caustic alkali under pressure. It forms a transparent non-crystalline mixture, which is soluble in water. If the proportion of silica is increased the fusing point is raised, and the product is not completely soluble in water. It is used as a cement, especially in the making of artificial stone ; also as a constituent of paints, particularly the fireproof paints ; and it is sometimes put into soaps.

Glass.—The origin of glass-making is lost in antiquity. In Egyp- **477** tian tombs have been found articles of glass and pictures of men who are engaged in glass-making and glass-blowing, showing that the art must have been invented before 2000 B. C. An urn of white glass, ornamented with colored glass, dating from the seventeenth century B. C., has been found, and glass lenses have been discovered at Nineveh. Aristophanes, a Greek writer, refers to the use of a glass lens as burning glass. Cicero mentions Egyptian glass, and in the time of Augustus tribute was paid in glass, so highly was it valued. At Herculaneum and Pompeii window glass has been discovered which was made by " blowing." Glass was used in church windows as early as A. D. 674. In the sixteenth and seventeenth centuries Venetian glass, especially that of Murano, became famous throughout the civilized world. In the sixteenth century the Bohemian industry began to flourish, favored by the accessibility of unusually pure material. Bohemian glass is still preferred for chemical ware, owing to its resistance to corrosion by reagents. The famous plate-glass industry of France was started in 1688.

Glass is a mixture of silicates, varying only as to the bases. Soda- **478** lime silicate is used in window and in bottle glass, which, in the cheaper grades, is tinted green by the presence of iron. Potash-lime silicate is used in the Bohemian, in the German plate, and in the French crown glass. It is less fusible and less acted upon than the soda-lime glass.

In flint glass or crystal the base is lead and potash or soda. This variety has a higher specific gravity, luster, and refractive power, and is more fusible and more easily acted upon than the others.

479   For silica, sand is used, which for any but the cheaper grade of glass must be free of iron. Sometimes arsenious oxide, or manganese dioxide, or potassium nitrate is used to counteract the effect of the iron. The alkali, if potassium, is used as carbonate; if sodium, it is used as carbonate, or as the sulphate which is produced in one stage of the Leblanc process. The attempts to use the cheaper chloride have not been successful. The lead is supplied usually as red lead or minium, Pb_3O_4. For the lime either chalk or limestone is used.

480   Glass is made white and translucent by adding a mixture of tin and lead, or by adding arsenic or bone ash (calcium phosphate) or fluorides, such as calcium fluoride. Colored glasses are made by the addition of various metallic oxides in small quantity—blue by copper or cobalt; amethyst by manganese; green by a mixture of iron and copper; yellow sometimes by adding wood (i. e., carbon), sometimes by sulphur.

481   The process consists in heating the suitable mixture in pots of fireclay to a high temperature. Broken glass is usually mixed with the new material in order that fusion may be brought about without too high a temperature which causes waste of alkali before the reaction sets in. The escape of carbon dioxide, and of sulphur dioxide if sulphate is used, causes effervescence. After the reaction is complete the mixture is kept in fusion until the impurities come to the top and form the scum which is removed. The glass in a semi-solid or plastic condition is worked into the desired shape by many ingenious methods, which, however, do not involve chemical processes.

482   **Porcelain and earthenware.**—In the making of these materials, which also is a very ancient art, advantage is taken of two properties shown by the natural substance, clay; one is that of plasticity when wet, and the other is that of hardening by heat. Clay in its several varieties is the product by slow natural decomposition of the mineral *feldspar*, a common rock. Pure *feldspar* is a silicate of aluminium and sodium or potassium. By its decomposition the alkaline silicate is washed out and aluminium silicate is left. This substance is known as *kaolin*, and in some places is found very pure. It is greatly prized as material for the finer porcelains. Common clay consists of kaolin mixed with more or less of other substances—carbonates of calcium and magnesium, iron oxide, silica, etc. For fine porcelain the white powdered kaolin is mixed with some more fusible substances, such as feldspar, chalk, or gypsum (calcium sulphate), worked into plastic mixture with water,

formed into desired shapes, and heated in a furnace to high temperature, when the more fusible portion, the flux, melts and cements the whole into a hard, translucent material. This is less corroded by chemicals and less liable to crack by heating than is glass, and so is a material very useful for chemical operations. The factories of Meissen and of Berlin are famous for their chemical ware, while Sèvres and others are noted for artistic porcelains.

Stoneware is distinguished from porcelain in being opaque, for it is **483** not heated to so high a temperature, and the flux does not penetrate the material as in porcelain. *Earthenware* is of common clay and is hardened by heat without fusion, and therefore remains porous. The surface may be glazed by a subsequent operation. This is sometimes accomplished by throwing salt into the oven at the end of the firing. The salt volatilizes, is decomposed, and sodium aluminium silicate is formed and fused on the surface. Bricks, terra-cotta, and tiling are of the same general character (Roscoe and Thorpe). The use of sand in mortar and cement will be referred to in connection with calcium.

13. PHOSPHORUS

P.—30.8

History.—Phosphorus was discovered by the alchemist Brand, of **484** Hamburg, in 1669. For many years it remained a rare and costly curiosity. In 1771, Scheele, a Swede, made it from bone ash and greatly reduced the cost. This still remains the commercial source of the element.

Natural occurrence.—Free phosphorus is not found na- **485** tive, owing to its readiness of oxidation. As pentoxide, P_2O_5, it exists in all phosphates, particularly in the minerals *phosphorite* and *apatite*, which are phosphates of calcium. As such it is also a constituent of fertile soils and of natural waters. It is an essential element in plants, being contained especially in fruits and seeds. In animals it is a part of the brain and nerve substance, and, as calcium phosphate, constitutes nearly the whole of bone ash. It is a waste product of the tissue which is consumed in the animal organism, and it is excreted as sodium ammonium phosphate. It has been found in meteoric stones.

485/1   Preparation.—Phosphorus is prepared by removing the oxygen from the pentoxide contained in a phosphate. The reducing substance is commonly carbon. For more detailed description see No. 499.

486   Properties.—It exists in at least two allotropic forms, commonly designated as the yellow and the red. The so-called *yellow* phosphorus, before it has been exposed much to the light, is white and translucent, somewhat like paraffin in appearance. By exposure, the surface film becomes opaque, while the interior may still be translucent, but reddish yellow. By long exposure the color deepens. At about 15°, phosphorus in hardness and consistency resembles wax, but at lower temperature it is brittle. Its specific gravity is 1.8 ($H_2O = 1$). For its peculiarity of vapor-density compare No. 93. Under water it melts at 44°, but otherwise at 30°, and at 34° in air it takes fire. It sublimes at ordinary temperature, if in a vacuous tube, and forms white rhombic crystals. In a non-oxidizing atmosphere it boils at 269°, and its vapor is colorless (Readman-Thorpe). It is reckoned as insoluble in water, yet it imparts its peculiar odor to water in which it has been immersed; and if the water which covers the phosphorus is boiled, the latter slowly distills with the steam. It is very soluble in carbon disulphide, from which it may be crystallized.

487   It ignites, as already stated, at a very low temperature, and burns with a bright, white light, the chief product being P_2O_5. It is necessary to keep it and manipulate it under water, and the utmost caution against fire must be exercised in its use. When exposed to moist air it gives out a feeble light which may be seen in a darkened room. Indeed, it took its name, signifying light-bearer, from this

488   property which is called *phosphorescence.* It is supposed to be due to slow oxidation, but, singularly, it does not show in absolutely dry air, nor in moist air, below 0°, or at increased pressure, nor in pure oxygen below 15°, if at ordinary pressure; but if the pressure is reduced, luminosity returns.

The phosphorescence is thought to be somehow associated with the formation of ozone (or of peroxide of hydrogen), since it is prevented by the presence in traces of such substances as destroy ozone. It decomposes water when heated with steam to 250°. It combines directly with fluorine, chlorine, bromine, iodine, forming PF_3, PF_5, PCl_3, PCl_5, PBr_3, PBr_5, and PI_3; also with sulphur in a great variety of proportions, including P_2S_3 and P_2S_5; with most of the metals, forming phosphides, e. g., Na_3P and K_3P. No compound with carbon nor with silicon is known, and the existence of one with nitrogen is not fully established. With hydrogen, PH_3 and others are known.

489 Phosphorus (the yellow) is extremely poisonous, one tenth of a gram proving fatal. In much smaller doses it is used as a medicine. Those who are habitually exposed to its fumes are subject to a dreadful disease which results in the rotting of the bones of the jaw and nose. Burns made by it are very painful and difficult to heal.

490 *Red phosphorus.*—When the yellow phosphorus is heated, not in contact with oxygen, to 240° or 250,° it is changed to an allotropic form known as red or amorphous phosphorus. A lower temperature brings the same result if a trace of iodine is present, and a higher temperature and pressure hasten the change. Other conditions also bring it about to some extent. It appears as a reddish-brown powder, or in hard, brittle, opaque lumps of the same color. It may be crystallized by heating under pressure to 580°, when it melts and, on solidifying, crystallizes. It has no odor, and does not fume nor phosphoresce. It does not dissolve in carbon disulphide nor in other solvents. Its specific gravity is 2.25.

491 At about the temperature of its production, 260°, it changes back to the yellow form with the liberation of heat. It does not ignite below 240°, and is much less reactive than the yellow. It is not poisonous, being excreted apparently without absorption or change.

13a. *The Oxides of Phosphorus and their Acids*

492   The following oxides and acids have been described :

Oxides.	Acids.
P_4O	No acid.
P_2O *	$P_2O \cdot 3H_2O$, hypophosphorous acid.
P_4O_6	$P_2O_3 \cdot 3H_2O$, phosphorous acid.
P_2O_4	$P_2O_4 \cdot 2H_2O$, hypophosphoric acid.
P_4O_{10}	$P_2O_5 \cdot 3H_2O$, phosphoric acid.

The only ones which call for consideration here are the phosphorous or trioxide, and the phosphoric or pentoxide.

493   **Phosphorous oxide,** P_4O_6.—This is formed by the slow oxidation of phosphorus at low temperature, and by the burning of phosphorus with insufficient oxygen ; and it is separated by its greater volatility from the pentoxide which is formed at the same time. It is a white crystalline solid, which melts at 22.5° and boils at 173°. Its vapor-density indicates the formula P_4O_6. It has the garliclike odor which is associated with phosphorus, and it is very poisonous. With cold water it slowly combines, forming phosphorous acid, H_3PO_3 ; with hot water it combines violently, with some decomposition. By heating to 440°, it is entirely decomposed into the tetroxide, P_2O_4, and red phosphorus. By slight warming in contact with air it inflames, burning to the pentoxide.

494   **Phosphoric oxide,** P_4O_{10}.—This is a white, odorless, amorphous solid, volatile below red heat. Its vapor-density indicates the formula P_4O_{10} (Tilden, 1896). It is extremely deliquescent, being the most effective drying agent known. With water it forms at least three different acids. By deliquescence in moist air *metaphosphoric* acid is formed. This, by boiling with excess of water, yields *orthophosphoric*

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* Besson, Comptes Rendus, 124, 1897.

acid, and this in turn, by evaporating the excess of water and heating the acid to about 215°, is converted, although not completely, into the *pyrophosphoric* acid. The relation of the three acids may be seen in the following equations:

$$P_2O_5 + H_2O = H_2P_2O_6, \text{ metaphosphoric acid.}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7, \text{ pyrophosphoric acid.}$$
$$P_2O_5 + 3H_2O = H_6P_2O_8 = 2H_3PO_4, \text{ orthophosphoric acid.}$$
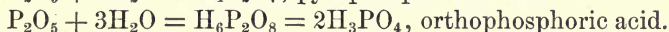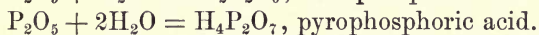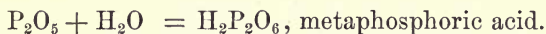
Orthophosphoric acid may be obtained in crystallized **495** condition by the evaporation of its water solution, and the pyrophosphoric may be obtained in the form of an amorphous, glasslike substance, or it may be crystallized. Both are non-volatile (?). The metaphosphoric acid appears in commerce as a white, glasslike solid, called "glacial phosphoric acid." It is volatile at a bright-red heat, and its vapor-density indicates the formula $H_2P_2O_6$ (Tilden, 1896). All these acids form salts, the most important being the orthophosphates, and of these the calcium salt is perhaps the most important. The hydrogen of the orthophosphoric acid, H_3PO_4, may be substituted by metal in thirds at a time, so that with sodium, for example, the three salts are obtained, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4.

13b. *Other Compounds of Phosphorus*

Hydrides.—That hydrogen and phosphorus combine **496** directly has been stated and denied. However, the compound, PH_3, phosphorus *trihydride*, or *phosphine*, or phosphureted hydrogen, has been obtained by other means. It is formed by the action of water on some metallic phosphides, as ammonia is formed by the action of water on some metallic nitrides; also by boiling phosphorus with sodium or potassium hydroxide solution. It is a gas with a garliclike odor, only slightly soluble in water, easily combustible, with no action on litmus, but acting as a feeble base in combining with some acids—e. g., hydrochloric,

forming a salt, PH_3HCl, analogous to ammonium chloride, NH_3HCl, and named *phosphonium* chloride.

Another hydride, P_2H_4 (compare N_2H_4), is a liquid at ordinary temperature, and its vapor inflames on contact with air. A third (P_4H_2?) of undetermined composition is solid at ordinary temperature. The existence of another solid hydride, P_3H, has been claimed by some.

497   Chlorides.—The trichloride, PCl_3, is a colorless liquid, and the pentachloride a yellowish solid. Both are formed by direct union with chlorine, and both react energetically with water, forming phosphorous and phosphoric acids :

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$
$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$
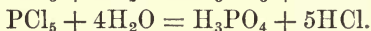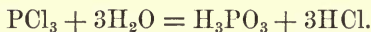
13c. *The Manufacture of Phosphorus and of Matches*

498   The crude phosphates.—Commercial bone ash contains from 27 to 37 per cent of phosphorus pentoxide as tricalcium phosphate, $Ca_3(PO_4)_2$, a salt insoluble in water. This material is especially preferred in making phosphorus. A similar crude phosphate is obtained as a by-product in making glue; for the bones are treated with dilute hydrochloric acid, which dissolves out the inorganic portion, $Ca_3(PO_4)_2$, leaving the organic part, from which the glue is made. From this acid solution, calcium phosphate is precipitated by adding limewater. The native calcium phosphates, more or less impure, known as apatite and phosphorite, are available. The former is found in Spain, France, West Indies, Canada, South Carolina, Florida, and elsewhere. A phosphate of aluminium and iron from the West Indies is another source.

499   Phosphorus-making.—Whatever the crude material, it is finely ground and mixed with crude sulphuric acid in vats made of wood, heavily oiled for protection. Sufficient acid is added for the following reaction :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4.$$
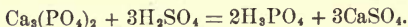
After the mixture has been thoroughly stirred for some time, the insoluble calcium sulphate is separated by filtration through beds of ashes, is washed with water, and then drained and dried. It is technically known as "sludge," and is used in making fertilizers. The acid liquor is concentrated, mixed with coarsely ground charcoal or coke, or with sawdust, and still further dried. It is then transferred to

retorts of fire-clay, holding from 20 to 30 pounds, and brought to a high temperature, nearly white heat. The orthophosphoric acid is thus first converted into the meta acid, and this is reduced by the carbon as thus expressed:

$$H_2P_2O_6 + 6C = 2P + 6CO + 2H.$$
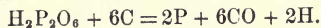
The phosphorus distills from the retort, and is condensed under water. **500** It is purified by redistillation in an iron retort, or by treatment under water with dilute sulphuric acid and potassium bichromate, and filtration through canvas. It is then remelted and cast in desired form, always under water, and packed in tin cans, which are filled with water and hermetically sealed.

A more recent method, made practicable by cheapened electricity, **501** uses the latter as source of heat in a modified electric furnace. The mixture of crude phosphate, carbon, and a flux (kaolin or sand), is fed into the furnace and heated directly by the electric arc; the phosphorus and other gases are distilled off, and the melted residue or slag is drawn off at the bottom. The process may thus be carried on continuously for days. Phosphorus is largely consumed in the manufacture of matches. In smaller quantity it is used in medicine, in the laboratory, and in various other ways. (Readman-Thorpe.)

Fertilizers.—It has been stated that phosphate is a constituent of **502** fertile soil, being taken up by plants as a necessary part of their food. It is important, therefore, to restore to the soil that which is thus taken from it. This is done by phosphate fertilizers which supply calcium phosphate in one form or another. Besides the phosphates already mentioned as crude material in preparing the element, the phosphates from some other sources are utilized. *Guano* is the excrement and carcasses of sea fowl, more or less modified by time and exposure. It is found in large deposits in Peru, Chili, and in other portions of South America, in South Africa, and elsewhere. From some of this material, the nitrogenous content has been washed out and the residue is rich in calcium phosphate, sometimes containing as much as 35 per cent of the pentoxide. *Phosphatic slag* is a waste material produced in the removal of phosphorus from pig-iron by means of lime. This contains from 10 to 25 per cent of pentoxide, mainly as the calcium salt, and has been successfully utilized as fertilizer. Practically all of these crude **503** materials furnish only the tricalcium phosphate, $Ca_3(PO_4)_2$, which is insoluble in water. Some of them, especially the guanos, slag, and bone ash, may be applied to the soil without other treatment than pulverizing. But others, like the rock phosphates, are treated with sulphuric acid after fine grinding, and the phosphate is changed to the monocalcium salt which is soluble in water, and therefore more quickly and

uniformly distributed through the soil and taken up by plants.   The reactions involved are seen in the following equations:

$$(1)\ Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$
$$(2)\ Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4.$$
$$(3)\ Ca_3(PO_4)_2 + H_2SO_4 = Ca_2H_2(PO_4)_2 + CaSO_4.$$
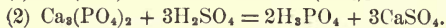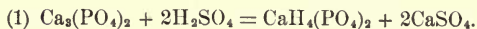
The aim is to bring about the first reaction chiefly, but the second is allowed to take place to some extent.   The dicalcium salt is insoluble, and therefore nothing is gained by the third reaction.   The soluble salt produced in the process is called technically *superphosphate*.   Before using the sulphuric acid, the crude material is dried and very finely powdered.   It is then thoroughly mixed with the acid in suitable quantity.   After the reaction is over, the mixture solidifies.   It is further dried at about 105° and again ground to powder, when it is **504** ready for the market.   The product on keeping is subject to a change called "reversion," which takes place if iron oxide or alumina is present, and the result of which is that the soluble phosphate passes back into the tricalcium salt, and insoluble phosphate of iron or of aluminium is produced.   These, although not useless, are less valuable than the superphosphate (Warington-Thorpe).

505   **Matches.**—Phosphorus was first used for making matches, according to some, in 1805 in Paris.   By others it is stated that the first friction matches containing it were made in 1816, also in Paris.   Other chemical methods of getting fire had been devised, but without general success, and the method by friction of flint and steel was the only one in general use up to 1820, and indeed was not entirely displaced so late as 1840.   The "Lucifer match" in its original form, invented by an Englishman in 1827, contained no phosphorus, the splints of wood being tipped with a mixture of antimony sulphide, potassium chlorate, gum, and starch, and ignited by rubbing on glass or sandpaper.   The first attempts to use phosphorus were not very successful, but in 1834 the German makers reached better results and phosphorus friction matches came into more general use.   An improvement made in 1835 consisted in using red lead, Pb_3O_4, and manganese dioxide, MnO_2, as oxidizing material with the phosphorus.   The first patent of this kind in the United States was granted in 1836 for a mixture of phosphorus, sulphur, chalk, and glue.   The manufacture rapidly increased, and the danger of accidental ignition of phosphorus mixtures, and the terrible disease which made its appearance among the workers in phosphorus, attracted great attention.   Investigation showed that the latter was probably due to the direct action of the fumes of phosphorus (i. e., P_4O_6) on the bone itself, and that it attacked only those whose teeth were decayed.   As a

result, improved ventilation, cleanliness, and strict attention to sanitary conditions have almost eliminated the disease. After the discovery of **506** red phosphorus in 1845, attempts were quickly made to take advantage of its non-poisonous character and less inflammability by substituting it for the yellow variety. In 1855, and in Sweden, the first "safety matches" were made. The invention consisted in putting the oxidizing mixture on the match head, and the red phosphorus on the box surface. The match could be ignited only by friction on the latter. One recipe gives for the mixture on the match head, antimony sulphide 8 parts, potassium chlorate 8 parts, red lead 8 parts, and gum 1 part; on the rubber, red phosphorus 1 part, antimony sulphide 7 parts, glue 1 part, and powdered glass 3 parts. Such matches are now made in great quantity in Sweden. As typical of a match prepared to ignite without the specially prepared surface may be cited this recipe: Red phosphorus 1 part, potassium chlorate 6 parts, red lead 2 parts, glue 1 part, powdered glass 3 parts, clay 3 parts (Clayton-Thorpe).

14. SULPHUR

S.—31.83

Natural occurrence.—Sulphur, being quite common in the **507** free state, has been known from the earliest times. It is found in the neighborhood of extinct and of active volcanoes —e. g., in Italy, Sicily, California, and in the Yellowstone region. The native *sulphides* are abundant, many of the most common metallic ores being of this form—e. g., sulphide of iron (known as *pyrites*), of copper, lead, zinc, and mercury. Native *sulphates* also are common, such as sulphate of calcium (known as *gypsum*), of barium, and of magnesium. Volcanic gases often contain sulphur dioxide, and some contain hydrogen sulphide. Besides this, sulphur is a constituent of many substances of plant and of animal origin—e. g., mustard, garlic, bile, albumin, and protoplasm itself.

Preparation.—Native sulphur is refined by fusion or by **508** distillation, and comes into commerce as *roll* sulphur or *brimstone*, as sulphur *flowers* (the sublimate), and as *milk* of sulphur (precipitated sulphur).

509   **Properties.**—Sulphur exists in at least three allotropic forms—the rhombic, the monoclinic (referring to crystalline form), and the plastic.

509/1   *Rhombic or common sulphur.*—Sulphur in this form is deposited by crystallization from solution in carbon disulphide. It is yellow, has the specific gravity 2.05, is insoluble in water, and melts at 114°.

509/2   *Monoclinic sulphur* is obtained by crystallization from fusion, and from solution in some solvents. Its specific gravity is 1.96, and it is soluble in carbon disulphide. This form is not stable at ordinary temperature, but changes into the rhombic; as a result, the crystals, which are at first clear and transparent, become opaque, owing to their breaking up into minute crystals of the other variety, although the external form is preserved. This change is accompanied by the liberation of heat. On the other hand, the rhombic crystal is similarly changed into monoclinic when kept at a temperature between 100° and 114°.

509/3   *Plastic sulphur.*—Sulphur melts to an amber-colored liquid, which, as the heating is continued, becomes of a dark-red color, and suddenly changes to a thick, semi-solid condition. On further heating, it again liquefies and finally begins to boil. If at this stage it is suddenly cooled by pouring into water, it becomes a transparent, plastic, rubberlike substance. This is the amorphous or plastic sulphur. It is not stable, but changes in a few hours, or quickly if warmed to 100°, back to the brittle, common form. The plastic allotrope has the specific gravity 1.95, and is insoluble in carbon disulphide. Some describe another allotrope, which is white, amorphous, present in the sublimate, but not soluble in carbon disulphide, and convertible at 100° into the common form; and still another which is soluble in water.

509/4   Sulphur, of all varieties, boils at 446°, and gives an orange-colored vapor. The peculiarities of its specific gravity in gaseous condition have been elsewhere described

(see No. 93). It ignites easily and burns with a pale-blue flame; the product of combustion is the dioxide, SO_2. Sulphur combines directly also with hydrogen, boron (B_2S_3), carbon (CS_2), chlorine, bromine, iodine, and probably fluorine, with phosphorus, and with many metals; in addition, compounds with nitrogen (N_4S_4), and with silicon (SiS) and (SiS_2), are formed, although not by direct action.

14a. *Compounds with Hydrogen and with Chlorine*

Hydrogen sulphide, or hydrosulphuric acid, or sulphureted hydrogen, H_2S.—This substance occurs native to some extent in volcanic gases, in mineral waters, and as a product of the decay of sulphur-containing organic substances. It is formed by direct union of hydrogen and sulphur vapor, and by the action of nascent hydrogen from acid and metal on finely divided sulphur suspended in water (Schützenberger); also by the action of acids on metallic sulphides such as those of iron and zinc; or, in purer condition, from antimony sulphide, Sb_2S_3, and hydrochloric acid. The action on sulphides is the common laboratory method of supply. **510**

Hydrogen sulphide is a gas without color, but with a marked odor, usually described as that of rotten eggs. The substance of the egg, since it contains sulphur, produces hydrogen sulphide in putrefying. The gas is condensable to a liquid which boils at $-62°$ and freezes at $-85°$. One volume of water dissolves about 3.5 volumes of the gas at ordinary temperature. The solution reddens litmus and slowly decomposes, precipitating sulphur. The gas, too, is separated into hydrogen and sulphur by heating to 400°. It is combustible, and with air may make an explosive mixture. It is extremely poisonous to inhale. Exposure to air containing even a small quantity of it is likely to produce headache. It reacts with many metals and with their salts in solution, producing metallic sul- **511**

phides, and in this way is much used as a laboratory reagent.

512 The *metallic sulphides* are salts of this acid, although made also by direct union of metal and sulphur. The gas, its water solution, and the sulphides show a marked tendency to combine with oxygen; they act, therefore, as reducing agents. A hydrogen *persulphide* of undetermined composition, H_2S_{1+}, and many metallic *persulphides*—e. g., CaS_2—are known. Such persulphides, when decomposed by an acid, generally yield hydrogen sulphide and sulphur.

513 Of *sulphur chlorides*, there are known S_2Cl_2, SCl_2, and SCl_4. The first is a fuming liquid, made by direct action of chlorine gas on melted sulphur. It finds some industrial use— e. g., in refining sugar, and in making India-rubber goods.

14b. *The Oxides of Sulphur, and the Acids of Sulphur containing Oxygen*

514   Of these substances the following are known :

(1) The sesquioxide, S_2O_3.
(2) The dioxide, SO_2.
(3) The trioxide, SO_3.
(4) The peroxide, S_2O_7.
          Hyposulphurous acid, H_2SO_2 (?).
    (2) Sulphurous acid, H_2SO_3.
    (3) Sulphuric acid, H_2SO_4.
        Thiosulphuric acid, $H_2S_2O_3$.
        Pyrosulphuric acid, $H_2S_2O_7$.
    (4) Persulphuric acid, $H_2S_2O_8$.

The oxides 2, 3, and 4 with water form the acids which are correspondingly numbered. Of these, only the second and third need be considered.

515   **Sulphur dioxide** (SO_2).—This is formed by the burning of sulphur and of substances containing unoxidized sulphur, and by the action of hydrochloric or other acid on sulphites; also by the removal of oxygen from sulphuric

acid, $H_2O \cdot SO_3$. These methods are sufficiently explained by the following equations :

$$S + 2O = SO_2.$$
$$Na_2SO_3 + 2HCl = SO_2 + H_2O + 2NaCl.$$
$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O.$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$
$$Cu + 2H_2SO_4 = SO_2 + 2H_2O + CuSO_4.$$
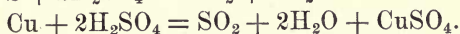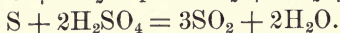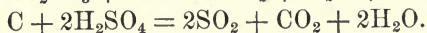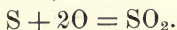
516 Sulphur dioxide is at ordinary temperature a gas without color, but with marked odor, and is extremely irritating to inhale. Its specific gravity is 31.97 ($H = 1$) or 2.2 (air $= 1$). In liquid form it boils at $-8°$ and freezes at $-76°$. One volume of water dissolves about 40 volumes of the gas at ordinary temperature, and loses it by boiling. The solution reddens litmus and contains sulphurous acid, H_2SO_3. The gas is not combustible, nor does it support ordinary combustion, although finely divided iron, tin, and potassium burn in it, forming both oxide and sulphide. It combines directly with oxygen to form the trioxide. It acts upon many coloring substances in the presence of water, destroying the color, and is used largely as a bleacher. In some cases the color is restored by time and by treatment with dilute acid or alkali. It is also an effective antiseptic, being used in preserving meat ; and as a disinfectant and germicide it is used in fumigating clothing and habitations to prevent the spread of disease. It is also used in paper-making, tanning, and in refining sugar. The liquid substance is supplied in commerce to some extent.

517 The *sulphites* are both normal and acid—e. g., Na_2SO_3 and $NaHSO_3$; and, like the acid and the gas, they act as reducing agents, by virtue of the tendency to form the trioxide, SO_3, and its compounds.

518 **Sulphur trioxide.**—This oxide is formed when a mixture of the dioxide and oxygen is passed over hot platinum or other substances which favor oxidation. It is also formed to some extent when sulphur is burned in oxygen. From

sulphuric acid, $H_2O \cdot SO_3$, it is obtained by the dehydrating action of phosphorus pentoxide, and from the pyrosulphuric acid, $H_2SO_4 \cdot SO_3$, or pyrosulphates simply by heating. It is a white crystalline solid which melts at 15° and boils at 46°. It fumes strongly when exposed to moist air, since its vapor, combining with moisture, produces the less volatile sulphuric acid. When the solid comes in contact with water, combination takes place with great energy. It is capable even of removing the constituents of water from many things—e. g., wood, paper, and the skin—and therefore it chars them as fire does. It combines directly with some metallic oxides forming sulphates—e. g., $BaO \cdot SO_3$. It is decomposed at red heat into the dioxide and oxygen. It has some industrial use, particularly in making dye-stuffs.

519   **Sulphuric acid,** $H_2O \cdot SO_3$, or H_2SO_4, is formed by the oxidation of sulphurous acid and by the direct combination of the trioxide with water. The substance whose composition is exactly represented by $H_2O \cdot SO_3$ is called *monohydrated* sulphuric acid. It is a colorless dense oily liquid, of the specific gravity 1.85. It easily solidifies to crystals which melt at 10.5°. When boiled, it gives off the trioxide until the temperature reaches 338°, when the latter remains constant, and an acid containing 98.5 per cent of H_2SO_4 passes over continuously. And dilute solutions of the acid by boiling lose water and become concentrated until a liquid of this same composition is reached, when the liquid itself passes over, giving the same distillate of 98.5 per cent acid.

The monohydrated acid still combines with water very energetically, even removing it, like the trioxide, from other substances and charring them. The maximum of heat is liberated when the ratio of acid to water is represented by $H_2SO_4 + 2H_2O$. The hydrate, $H_2SO_4 \cdot H_2O$, has been obtained in crystals melting at 8°; and another, $H_2SO_4 \cdot 4H_2O$, which melts at −25°. Pyrosulphuric acid, $H_2SO_4 \cdot SO_3$, or $H_2O \cdot 2SO_3$, is known also as *fuming* or *Nordhausen* sulphu-

520   ric acid. It is made by dissolving the trioxide in the ordi-

nary acid, and, commercially, by decomposing crystallized iron sulphate at high temperature, as thus expressed:

$$2FeSO_4 \cdot H_2O = Fe_2O_3 + SO_2 + SO_3 + 2H_2O.$$
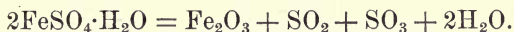
The acid, $H_2SO_4 \cdot SO_3$, has the specific gravity 1.88 and melts at 35°.

The ordinary *sulphates* are salts of the monohydrated **521** acid, H_2SO_4, but salts corresponding to the other hydrates are known. The former are among the most common and important of all salts. They are of two types, the normal and the acid salts—e. g., sodium sulphate, Na_2SO_4, and sodium acid sulphate, $NaHSO_4$.

The *thiosulphates* are salts of thiosulphuric acid, $H_2S_2O_3$. **522** The most common one is the sodium salt, $Na_2S_2O_3$, which is used in photography as a solvent for silver chloride and bromide. It is more familiarly known under the incorrect name of sodium *hyposulphite*.

14c. *The Manufacture of Sulphuric Acid*

The first record of making sulphuric acid is that of Valentine in **523** the last half of the fifteenth century, although the substance was known as early as the tenth century. His method was by heating green vitriol (iron sulphate), and the substance was called "oil of vitriol," or "vitriolic acid." The former name is still used somewhat in commerce. About 1740 the method of burning sulphur in connection with potassium nitrate was used on a small scale by Ward in England, and this has developed into one of the most important and extensive of the industries based upon chemical processes; the product is consumed in great quantity and for a great variety of purposes. The method of making consists essentially of three steps: First, producing sulphur dioxide by burning sulphur; second, changing this by means of nitrogen oxides to sulphur trioxide, and combining the latter with water; third, concentrating and purifying the product.

1. The crude material for making the dioxide is preferably sulphur, **524** but the cheaper iron pyrites (FeS_2), when it contains as much as 35 per cent of sulphur and also other sulphides, are largely used for the impurer grades of acid. Arsenic coming from the pyrites is often an impurity of this product. The combustion is accomplished in furnaces

with a carefully regulated supply of air, and generally without other fuel than the sulphur itself.

525   · 2. In connection with the furnace are placed the "niter pots," into which is placed a mixture of sodium nitrate and sulphuric acid in such proportion as to form the acid sulphate, $NaHSO_4$, and liberate the nitric acid. The hot gases from the furnace volatilize the nitric acid, which, mixing with the dioxide and steam, gives rise to reactions which may in their general character be represented by one or both of the following equations:

$$2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + N_2O_3.$$
$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$
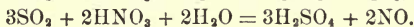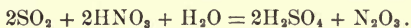
The mixed gases are carried into large chambers lined with sheet lead, and into these steam is injected. The exact nature of the reactions taking place is much disputed. They are undoubtedly complicated, but the result is simple enough. The nitric oxide is reoxidized to the higher oxide by contact with the oxygen of the air; this in turn gives up oxygen to more sulphur dioxide, is reduced, again oxidized, and so on indefinitely. Thus a comparatively small quantity of nitrogen oxide acts as carrier of a large quantity of oxygen from the air to the sulphur dioxide. The sulphuric acid forms as a mist in the chambers, which settles to the floor and is drawn off as a liquid containing about 68 per cent of sulphuric acid. To prevent the waste of nitrous fumes, the gases at their exit from the series of chambers are passed from the bottom to the top of a tower, which is loosely filled with lumps of coke. Over these, trickles sulphuric acid, somewhat more concentrated than that of the chambers. This acid dissolves the nitrogen oxides, forming an unstable compound, and the liquid is conducted from the base of this tower to the top of another similar one. In its passage down the latter it is brought in contact with the hot mixed gases coming from the furnace and on their way to the chambers. Under these conditions the nitrogen oxides are given up, and contribute to the oxidation of the sulphur dioxide. There is some loss of nitrogen oxides through imperfect absorption in the tower, as well as by secondary reactions in the chambers.

526   3. The product is further concentrated by heating in glass or platinum retorts until acid of 93 or 95 per cent is obtained (oil of vitriol), although the process may be carried on until 98 per cent is reached. By cooling such acid to −20°, it crystallizes; the crystals are separated and drained by pressure, then melted, and an acid of 100 per cent is obtained. Commercial acid is likely to contain lead sulphate in solution, which is precipitated when the acid is diluted. It is purified by redistillation,

15. CHLORINE

Cl.—35.18

History.—The substance now known as chlorine was first obtained **527** by Scheele in 1774 from hydrochloric acid and manganese dioxide, but it was regarded as a compound until Davy in 1810 proved it to be an element, and suggested its name, signifying greenish-yellow.

Natural occurrence.—It is not found free, but as a con- **528** stituent it is abundant in many native chlorides. In sodium and potassium chlorides it comes into important relation with the plant and animal organism.

Preparation.—The purely chemical methods of making **529** chlorine obtain it from hydrochloric acid by oxidizing the hydrogen to water and thus liberating the chlorine. The methods differ chiefly as to the means of effecting the oxidation. The hydrochloric acid itself must come from a native chloride, commonly that of sodium. It will be recalled that this acid is a by-product in the Leblanc soda process, therefore the chlorine manufacture is usually associated with the former. As oxidizing material, potassium chlorate, $KClO_3$, red lead, Pb_3O_4, potassium dichromate, $K_2Cr_2O_7$, manganese dioxide, MnO_2, and the oxygen of the air are used. In the laboratory, potassium chlorate and manganese dioxide are the most convenient. When the former **529/1** is used the general character of the reaction may be seen in the following equation:

$$KClO_3 + 6HCl = KCl + 3H_2O + 6Cl.$$
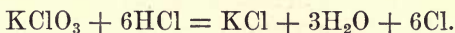
When the latter is used the final result is such as indicated by the equation:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$
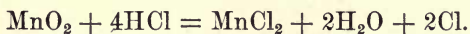
This result is in consequence of the fact that the only stable chloride of manganese is the one corresponding to manganous oxide, MnO, which with hydrochloric acid forms manganous chloride, $MnCl_2$, and water, with no liberation

14

of chlorine.   Any higher oxide, therefore, yields an excess of oxygen which is capable of oxidizing the hydrogen of the acid.   In order to liberate chlorine, the mixture of acid and oxide is heated, by which any higher chloride, if temporarily formed, as has been thought, is broken up into the dichloride and chlorine.   The manufacture of chlorine on the commercial scale will be described in a later section.

530   **Properties.**—Chlorine is a greenish-yellow gas of peculiar and disagreeable odor, intensely irritating, and poisonous if inhaled in quantity.   It is about 2.5 times heavier than air, and condenses to a liquid which boils at $-33.6°$ and freezes at $-102°$.   One volume of water dissolves about 2.2 volumes of the gas in ordinary conditions.   The water solution is not stable, for hydrochloric acid is slowly formed and oxygen liberated.   When the solution is cooled nearly to $0°$, a crystallized hydrate, $Cl·5H_2O$, separates.   It is much less soluble in a solution of sodium chloride than in pure water.

531   Chlorine is markedly reactive, but less so than fluorine. It does not burn in air, although compounds with oxygen exist.   In an atmosphere of hydrogen it burns readily, and a mixture with hydrogen in equal volumes ignites explosively; indeed, a ray of sunlight or of magnesium light is sufficient to provoke explosive combination in the mixture. The product in all cases is hydrochloric acid.   Chlorine removes hydrogen from other substances besides water, especially from organic substances; in consequence a lighted candle continues to burn in chlorine gas, for the material of the candle contains carbon and hydrogen; with the latter the chlorine combines, and the carbon is seen in the dense black smoke.   Some such organic substances—e. g., turpentine—inflame spontaneously in chlorine gas.   For the same reason chlorine acts as a powerful bleacher, often destroying the coloring substance.   Under some conditions the chlorine not only removes hydrogen from a compound, but in addition takes its place as constituent

(substitution). This is illustrated in the reaction with benzene, C_6H_6, thus :

$$C_6H_6 + 2Cl = C_6H_5Cl + HCl.$$
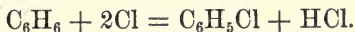
Associated with water, chlorine is an active oxidizing **532** agent, for it combines with the hydrogen and liberates nascent oxygen. For this purpose it is often used in the laboratory ; thus chlorine water with hydrogen sulphide liberates sulphur. These properties make it useful as a disinfectant and deodorizer. It combines directly, especially when moist, with most of the metals, and also with phosphorus, so that compounds exist with all the elements preceding it in the list, except fluorine.

Hydrochloric acid.—This substance, or its water solution, **533** was known as early as the fifteenth century, perhaps earlier, but Davy, in 1810, first proved that it contained only chlorine and hydrogen. It occurs free in some volcanic gases and in some natural waters. The native chlorides, as well as the preparation of the acid, have already been sufficiently considered. The anhydrous hydrogen chloride **534** is a colorless gas very irritating to inhale, and about 1.25 times heavier than air. Its boiling point is $-102°$, and freezing point $-112.5°$. It does not burn nor support combustion. It has strong tendency to dissolve in water, and probably to combine with it, so that the gas itself, or the vapor from a strong solution of it, fumes—that is, forms a mist or cloud when in contact with moist air ; this may be due to the formation of a less volatile hydrate. The gas is extremely soluble in water, one volume of the latter dissolving about 450 volumes of the gas at 18° and ordinary pressure. The solution has the specific gravity 1.2 and contains 42 per cent by weight of the anhydrous substance. When a solution is heated it loses water or acid, as the case may be, until the mixture has a specific gravity of 1.1 and contains 20 per cent of acid, and boils at 110° at ordinary pressure, when the solution distills without change. A

crystallized hydrate, $HCl \cdot 2H_2O$, separates on cooling a saturated solution to $-18°$.

535   The commercial article, often designated as *muriatic acid*, is a water solution containing about 40 per cent by weight of the hydrogen chloride. Various impurities are present, often sulphuric acid, and iron and calcium chlorides, and it is more or less yellow in consequence. The purified acid is colorless.

Hydrochloric acid is consumed in large quantity, chiefly in making chlorine, but also in making metallic chlorides and carbon dioxide, and for various minor purposes.

536   15a.   *The Oxides of Chlorine and their Acids*

Of these compounds the following are known:

Oxides.	Acids.
Cl_2O.	$HClO$, hypochlorous acid.
(Cl_2O_2) unknown.	No acid.
(Cl_2O_3) unknown.	$HClO_2$, chlorous acid.
ClO_2.	No acid.
(Cl_2O_5) unknown.	$HClO_3$, chloric acid.
(Cl_2O_7) unknown.	$HClO_4$, perchloric acid.

Chlorine and oxygen do not combine directly.

537   **The monoxide,** Cl_2O, is formed by reaction between dry chlorine and mercuric oxide at ordinary temperature:

$$2HgO + 4Cl = HgO \cdot HgCl_2 + Cl_2O.$$
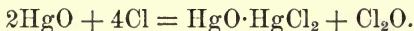
It is a yellow gas, of odor somewhat like that of chlorine, and condensable to a liquid which boils at $-20°$. The formation heat of the gas is $-17,800$ calories, and both gas and liquid are violently explosive on very slight provocation. One volume of water dissolves about 100 volumes of the gas and *hypochlorous acid*, $HClO$, is produced. The **538** acid solution also is unstable and can not be concentrated. It is a very active oxidizing and bleaching substance, readily splitting into hydrochloric acid and oxygen. With hydro-

chloric acid, water and chlorine are formed. Its salts, the *hypochlorites*, are more stable, but are decomposed by carbonic acid. When an alkali hydroxide in solution is treated **539** with chlorine in the cold, both chloride and hypochlorite are formed, thus :

$$2NaOH + 2Cl = NaCl + NaClO + H_2O.$$

The same formation takes place with solution of sodium carbonate. With calcium hydroxide (limewater), the reaction is—

$$2Ca(OH)_2 + 4Cl = CaCl_2 + Ca(ClO)_2 + 2H_2O.$$
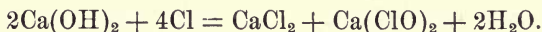
If excess of chlorine is present, the hypochlorous acid is liberated. Such solutions, made by treating with chlorine the hydroxide, or the carbonate, of sodium, or of potassium, or of calcium, are active oxidizers and bleachers, and have been much used for these purposes. The calcium hypochlorite has been obtained in crystallized condition. In the presence of small quantities of some substances—e. g., cobalt salt—hypochlorite, like the free acid, liberates oxygen:

$$Ca(ClO)_2 = CaCl_2 + 2O.$$
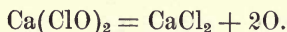
The peroxide.—This is the name generally given to the **540** substance ClO_2. It is formed, along with perchlorate, by the action of sulphuric acid on potassium chlorate :

$$3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + H_2O + 2ClO_2 ;$$
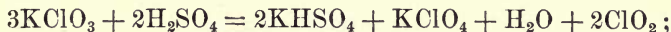
also by the action of a feeble reducing substance on chloric acid, $HClO_3$. It is a dark-red liquid which boils at 9° ; the gas is dark yellow, and has a specific gravity which indicates the formula ClO_2. It dissolves in water abundantly, probably forming chlorous acid, $HClO_2$, and chloric acid, $HClO_3$. This oxide, like the preceding, is very unstable, decomposing explosively, particularly if brought in contact with oxidizable matter. Some substances, like phosphorus and hydrogen sulphide, take fire in the gas at ordinary temperature.

541   Of *chlorous* acid, $HClO_2$, and the *chlorites*, nothing further need be said. *Chloric* acid, $HClO_3$, and *perchloric* acid, $HClO_4$, are likewise explosively unstable and very energetic oxidizers. Their salts are more stable than the free acids. Potassium and sodium chlorates have some industrial importance. They are formed by boiling the solutions of the hypochlorites, thus:

$$3KClO = KClO_3 + 2KCl.$$

Or, if chlorine is passed into hot solution of the hydroxide, this reaction takes place:

$$6KOH + 6Cl = 5KCl + KClO_3 + 3H_2O.$$

The chlorate is less soluble than the chloride, and is separated by crystallization. Practically, however, calcium chlorate is first produced by the action of chlorine on milk of lime, $Ca(OH)_2$, whereby the hypochlorite is formed. This, by heating with excess of chlorine, is converted into chlorate and chloride. Finally potassium chloride is added, and potassium chlorate crystallizes out on concentration. This substance is used in making oxygen gas, matches, fireworks, fuses, and some kinds of gunpowder and other explosives, and as oxidizer in the preparation of some of the dyestuffs. It is also used to some extent in medicine.

15b.   *Bromine and Iodine*

Br.—79.35.   I.—125.9

541/1   There is convenience of arrangement in briefly describing at this point the elements, bromine and iodine, Nos. 32 and 47 in the list. They are very similar to chlorine and fluorine. Neither is found free, but both occur native as constituents, chiefly in the bromides and the iodides respectively. Of these the sodium, potassium, calcium, and magnesium salts are the most common, occurring in sea water, in some mineral waters, and in sea plants. The

ashes of the latter are a commercial source. Their preparation is similar to that of chlorine. It consists in the liberation from bromides and iodides by the action of sulphuric acid and an oxidizing substance (e. g., MnO_2), and the subsequent purification by distillation. Bromine is a very volatile liquid, boiling point 59°, and iodine is a solid, melting point 114° and boiling point 184°. Bromine is of a dark red-brown color both as liquid and as vapor. Iodine is lustrous and almost black, and highly crystalline. It readily sublimes, and the vapor is reddish-violet. Both have marked odor, that of the former being especially disagreeable (hence its name signifying stench). Both dissolve readily in carbon disulphide and in some other solvents. Bromine is only slightly soluble in water, and iodine is still less so. Both are highly reactive, corrosive, and poisonous, the former more than the latter. Bromine displaces iodine in combination, and both are displaced by chlorine. They form compounds with most of the other elements, combining with many of them directly. No oxide of bromine has been obtained free, although it exists as a constituent. Of iodine the pentoxide, I_2O_5, is the only oxide whose existence in the free condition is known. They combine with hydrogen, less readily in the case of iodine, and the products are hydracids—viz., hydrobromic acid, HBr, and hydriodic acid, HI. The sodium and potassium salts of these are the most common. Bromic acid, $HBrO_3$, and iodic acid, HIO_3, and their salts are known, and hypobromites and hypoiodites probably exist, but are less stable than the hypochlorites. The four elements fluorine, chlorine, bromine, and iodine are often called the *halogens*.

15c. *The Manufacture of Chlorine and of Bleaching Powder*

Chlorine has considerable industrial use. Its applicability to bleaching was suggested as early as 1785 by Berthollet, and in 1789 the bleaching liquor known as "eau de Javel" was manufactured. This was practically a solution of potassium hypochlorite, and it made a

more available commercial article than the gaseous chlorine. In 1798 the cheaper material, lime, was used to prepare a similar liquor, which is still somewhat used. The use of dry calcium hydroxide, and the preparation of a "bleaching powder," was accomplished in 1799. This has the advantage of greater stability, although the material which is in the form of solution is more convenient, more concentrated, and cheaper. Quite recently chlorine itself in liquid condition, stored under pressure in steel cylinders, has come into commerce.

543   For *making the chlorine*, the reaction with manganese dioxide is largely used. The crude ore is *pyrolusite*, which may contain from 70 to 85 per cent of the dioxide, MnO_2. Sometimes a mixture of common salt and the dioxide is acted upon by sulphuric acid, but more commonly the hydrochloric acid from the Leblanc process is applied directly to the dioxide. The operation is carried on sometimes in stoneware retorts, heated from without by hot water ; sometimes in vessels built of stone slabs, into which steam is introduced for the necessary heating. The ore is used in coarse lumps, and is often contained in a sievelike vessel, or spread on a perforated raised bottom of the tank. The hydrochloric acid is admitted gradually. When the reaction is over, the liquid left in the generator, called the "still-liquor," contains principally manganese dichloride, $MnCl_2$, with considerable unused hydrochloric acid and some iron chloride, and it is still capable of liberating some chlorine. This was at one time allowed to go to waste, but as it must necessarily be a great nuisance, the disposal of it became a problem. It was finally discovered that from this material the manganese could be recovered and used over again. One method of accomplishing this was first brought into practical use in 1869, and is known as the Weldon process.

544   The *Weldon process*, so far as pertains to the chemical reactions, is as follows: The "still-liquor" is mixed with powdered limestone or chalk, $CaCO_3$, whereby the free acid is neutralized and the iron is precipitated. The precipitate is allowed to settle, and the clear solution of manganese and calcium chlorides is drawn off. To this solution is added milk of lime, until the manganese is all precipitated as hydroxide :

$$MnCl_2 + Ca(OH)_2 = MnO \cdot H_2O + CaCl_2.$$
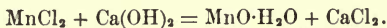
Then from one half to one quarter more lime is added for excess, and air, somewhat heated, is blown into the pasty mixture. The oxygen converts the manganese monoxide into the dioxide, which, acting as an acid, combines with the lime as a base, forming principally $CaO \cdot MnO_2$. The mixture is still in the form of a thin paste, and it is run into settling tanks, where the clear solution of calcium chloride separates and

is drawn off as waste. The manganese compound is technically known as " Weldon mud," and contains about 80 per cent of MnO_2. It is run directly into the chlorine generator, to be treated again with hydrochloric acid, and, being very finely divided, it is acted upon quickly and completely. The loss of dioxide is only 2 or 3 per cent, but only about one third of the hydrochloric acid is converted into chlorine.

The *Deacon process* obtains chlorine from hydrochloric acid by the **545** more direct action of oxygen from air. When a mixture of the two gases is heated, chlorine is liberated, but only slowly. In practice, the hydrochloric acid and air are heated to about 500° and passed over bricks which have been wet with a solution of copper chloride, $CuCl_2$, the presence of which greatly facilitates the liberation of chlorine, probably by reason of the alternate formation of copper oxide, CuO, and the chloride. From the resulting mixture of gases, the hydrochloric acid and water must be removed; the chlorine, mixed with nitrogen and oxygen, is then available for use.

Much effort is being expended to obtain practicable methods of **546** electrolyzing the solution of sodium chloride, as a means of producing both sodium hydroxide and chlorine, but the problem has not yet been satisfactorily solved.

The *bleaching powder*, or "chloride of lime," is produced by the **547** action of chlorine gas on slaked lime, $Ca(OH)_2$. The latter substance is prepared from "burned lime," CaO, by adding just enough, or very slightly more than enough, water to form the hydroxide and to leave it in the condition of a dry powder, which is carefully sifted. This is spread three or four inches deep on the floor of a chamber, generally lead-lined, and chlorine is passed in so long as the powder continues to absorb it. The product is a powder, nearly white in color, and of peculiar odor. It absorbs moisture and carbon dioxide and becomes pasty, losing at the same time some of its chlorine, and consequently deteriorating. It must, therefore, be packed in a way to protect it from the air, and from light which hastens decomposition. It is largely used to bleach materials in textile and paper-making industries, and it is one of the best disinfectants.

There has been much discussion as to the exact reaction between **548** the dry calcium hydroxide and the chlorine. It is now supposed that a substance, $CaOCl_2$, is formed and constitutes the bleaching powder, but is converted into hypochlorite when brought in contact with water:

$$2CaOCl_2 = Ca(ClO)_2 + CaCl_2.$$
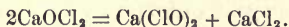
(Lunge-Thorpe and F. H. Thorp.)

16. POTASSIUM

K.—38.82

549   *History.*—The element potassium was obtained first by Davy in 1807 by the electrolysis of the hydroxide, although this compound and the carbonate had been known from the early days of alchemy.

550   **Natural occurrence.**—It is found only as constituent, but as such is quite abundant.   Its silicate is contained in granite, sometimes to the extent of 3 per cent, and also in many other rocks.   The chloride and sulphate are found in large deposits in the neighborhood of Stassfurt.   These salts are present also in sea water and in mineral waters. The occurrence of the nitrate (niter) in Chili and Peru has been mentioned in another connection.   Potassium compounds are present in fertile soils and are important in both the plant and the animal organism.

551   **The preparation** of potassium by the reduction of its carbonate and of its hydroxide, and by the electrolysis of its hydroxide, is so exactly similar to that of sodium that it need not be further described.   (Compare No. 409.)

552   **Properties.**—Potassium, like sodium, is a soft white metal. It melts at 62.5° and boils at 667°, a little lower than sodium. Its specific gravity is 0.86.   It oxidizes in moist air at ordinary temperature, and, when heated, burns energetically.   To the Bunsen flame it gives a violet color, as do its compounds.   It decomposes water at ordinary temperature, and carbon dioxide, when heated; it is, therefore, a power-

553   ful reducing agent.   As to *oxides*, it forms at least K_2O and K_2O_2.   The hydroxide is KHO; it is soluble and acts as a base, forming a series of well known salts, to several of which reference has already been made.   The chloride is KCl, and the nitrate is KNO_3, niter or saltpeter.   The

554   carbonate, K_2CO_3, is obtained from wood ashes and is manufactured from the chloride.   The reactions involved in this, as well as in making the hydroxide, are so similar to the corresponding ones for sodium, that they need not

be described. (Compare Nos. 414, 415, and 419.) The potassium compounds have various industrial applications; the hydroxide and carbonate, like the sodium compounds, are used in making glass and soap; the nitrate is largely used as a constituent of gunpowder, for which the sodium nitrate, owing to its being hygroscopic, is not available.

F. Gunpowder and Some Other Explosives

An explosive is a substance, or a mixture of substances, which by a **555** chemical change quickly generates gaseous products, the latter at the instant of their formation tending to occupy a much greater volume than the factors. The sudden conversion of water into steam may take place in a steam boiler and cause explosion, but no chemical change is involved, and water is not in this sense called an explosive. On the other hand, liquid acetylene may decompose explosively into carbon and hydrogen, and the volume of the hydrogen gas would be very much greater than that of the liquid acetylene. Furthermore, heat is liberated by the decomposition, and hence the gas would be considerably heated and tend to occupy a still greater volume. So, too, a mixture of hydrogen and chlorine explodes, although the volume of the product is only equal to that of the factors; but heat is liberated, and so the temperature, and therefore energy, of the product is suddenly increased. However, all the explosives in practical use liberate their energy by combustion; that is oxidation.

Gunpowder is one of the oldest of practical explosives, having been **556** used for firearms as early as 1346. It is a mixture of potassium nitrate, charcoal, and sulphur. The ingredients are carefully purified, finely ground, and very thoroughly mixed. The mixture, slightly damp, is put under heavy pressure—from 300 to 450 pounds to the square inch—in order to increase its density. The "press-cake" thus obtained is broken into small grains—"granulation" the process is called—and sifted. The grains are smoothed and glazed by rolling in wooden drums, sometimes with the addition of a little graphite. The product is again sifted, and freed of moisture by drying at a low temperature. A black powder, commonly used for military purposes, contains 75 per cent of potassium nitrate, 15 per cent of charcoal, and 10 per cent of sulphur. Some idea of the chemical change in the explosion is given **557** by the incomplete equation:

$$2KNO_3 + 3C + S = 3CO + 2N + K_2S + .$$
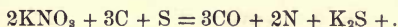
But it is actually, at least when taking place in a confined space, much more complicated. However, it is clear that the carbon and the sulphur may be converted into gaseous oxides by the oxygen of the nitrate, and thus combustion take place without the intervention of air to any extent. The large volume of the resulting gases and the heat liberated by the reaction cause the energy of the explosion. The gaseous products include:

Carbon dioxide, CO_2;
Nitrogen, N;
Carbon monoxide, CO;
Hydrogen sulphide, H_2S;
Hydrogen, H;
Methane, CH_4.

The hydrogen may come from the charcoal or from the moisture present. Of these gases, the first three make about 90 per cent of the total, while somewhat more than 90 per cent of the total solid products are made up of—

Potassium carbonate, K_2CO_3;
Potassium sulphate, K_2SO_4:
Potassium persulphide, K_2S_2.

558 The reaction is expressed with closer approximation by the equation,

$$8KNO_3 + 9C + 3S = 2K_2CO_3 + K_2SO_4 + K_2S_2 + 7CO_2 + 8N.$$
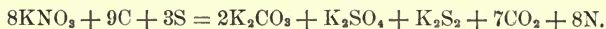
From 1 gram of powder the solid products weigh from 0.55 to 0.58 of a gram, and the gaseous from 0.45 to 0.42 of a gram, while the volume of the gases reckoned at 0° is from 200 to 300 cubic centimeters, and the temperature is estimated at 2,100° or 2,200°.

559 It is evident that the *rending effect* of an explosion must depend upon the rapidity of the reaction, for if the latter is slow the gases are slowly liberated, and the heat is gradually dissipated, so that the temperature does not rise as high; moreover, the pressure of expansion, which when suddenly applied may be irresistible, when slowly applied may be resisted. Now, if the reaction is one of oxidation the rapidity must be influenced by the closeness of contact, or intimacy of mixture, of the combustible with the supporter of combustion. It has been seen in the experiments (see Exp. 331/₁) that a piece of ignited charcoal burns actively, but not explosively, when brought in contact with melted nitrate. It is quite different if the two substances are finely powdered and then intimately mixed, as in gunpowder, each small grain of which contains its proportion of the three ingredients. Again, if the grains are made larger and therefore do not lie so closely in con-

tact, the rate of combustion through the whole mass, when the ignition is started at only one point, must be retarded. For this reason the powder used in heavy guns, known as "pebble" and "prismatic" powder, is made into grains which measure from five eighths to one and three quarters inches, so that the full pressure of the explosion is not reached at once. Were it otherwise, the gun might yield before the ball was set in motion.

Again, the *velocity* of combustion through a mass of gunpowder is **560** influenced by the pressure of surrounding gases. In a vacuum it does not explode at all, but burns slowly. In open air the ignition travels through the mass at the rate of four feet per second; in a heavy gun at about thirteen feet per second. So it happens sometimes, in using large-grained powder, that the charge is ignited and the ball leaves the gun before combustion reaches the last of the powder, and this is thrown out unburned. Likewise in exploding powder under water, if the containing case is not strong enough to hold the gases until the ignition is complete, a part of the charge may remain unexploded (Walke). By varying the quality of the charcoal, a "brown" or "cocoa" powder is made which is so slow in burning that a large grain may be ignited while held in the hand and dropped before the fire reaches the fingers.

Still again, the *velocity* of the combustion is influenced by the man- **561** ner of firing. In the foregoing statements it has been implied that the chemical reaction which produces the explosion is started by a suffi- cient rise of temperature in only a small portion of the powder, such as is practically caused by a spark of fire or a wire made hot by the electric current; and this ignition, producing heat and flame, spreads with more or less rapidity through the whole. But there is another mode of **562** firing, known as *detonation*. In this the reaction is brought about by the shock of another explosion and can not be due, at least not in all cases, to rise of temperature. A very common detonating material is mercury fulminate, the nature of which need not be explained here. Its application is seen in the ordinary percussion cap in which it is exploded by a blow, although when this is used in connection with powder the latter is probably fired by the small flame or spark from the cap, and so, strictly speaking, is not detonated. However, another explosive—namely, gun cotton—even when wet may be exploded by the explosion of a small quantity of fulminate in contact with it. In this case it can not be rise of temperature which explodes the gun cotton. This shock of detonation is brought to bear upon the whole mass of the explosive within the reach of its influence instantaneously, or at least with a rapidity very much greater than the velocity of ignition.

It is as if a violent blow were given to every minutest particle of the explosive at practically one instant of time, and therefore the explosion is made more violent. Gunpowder is not readily detonated; indeed, this method of explosion is not desirable for firing projectiles, and it is somewhat uncertain whether this material can be really detonated in any conditions. There is a class of explosives of altogether different chemical character which are most readily detonated. Before considering these, some modification in the constituents of gunpowder may be mentioned.

563   The nitrate of sodium, because of its cheapness, is substituted for the potassium salt in mining powder, especially when it is to be used in hot and dry countries. It was largely employed in building the Suez Canal, but its hygroscopic quality hinders its general use. The same objection applies to ammonium nitrate, although it has the advantage of producing a larger volume of gases and less solids, therefore less smoke.

564   Many attempts have been made to utilize potassium chlorate as oxidizing material. This decomposes at about 350° into potassium chloride and oxygen, with liberation of heat. A chlorate powder produces higher temperature and larger volume of gas, and simpler, less dissociable products; the reaction begins at lower temperature and spreads with greater rapidity, and therefore causes more abrupt and shattering effect than with nitrate powders. But the former are much more sensitive, and are subject even to (so-called) spontaneous explosion; therefore much greater danger attends their preparation, storage, and use. Besides, the products of decomposition are more corrosive of the gun and more injurious to the person than with the nitrate powders. The disadvantages overbalance the advantages, and have prevented the practical success of powder of this class for firing projectiles. But mixtures containing chlorate are used for charging explosive shells and bullets, and for fuses which are to be ignited by friction, percussion, or contact; in them, sugar and starch are sometimes used as the combustible material.

565   **Liquid mixtures.**—Some attempts have been made to use liquid mixtures of combustible and oxidizer, in which evidently the contact of the two would be more intimate than in the mechanical mixture of powders. One such mixture consists of nitric acid as oxidizer and solvent, and certain hydrocarbons as combustible. They seem to have no practical success.

566   **Gaseous mixtures** must bring the combustible and oxidizer into intimacy of the same order, as in liquids, reaching to the minutest particles of the substances—that is, to the molecules themselves. But,

from the very nature of the gaseous condition, it would seem that reaction by shock could not be brought about as in liquids and solids, and that the spread of the combustion must depend on temperature or inflammability. In combustion of this kind the volume of the products is not necessarily larger than that of the explosive mixture; indeed, it may be less, as when three volumes of hydrogen and oxygen become two of water. The explosive power then must be due to the rise of temperature in the gases, which is caused by the heat of reaction. Gaseous mixtures are not applied to the ordinary purposes of explosives, but they are often the cause of serious accidents, and they find a limited use as motive power in gas engines.

Another type of explosive mixture has likewise been the cause of **567** most serious accidents—namely, a combustible solid in the form of very fine dust scattered through the air in a more or less confined space. It will readily be understood that minute particles of carbon might be suspended in air so close to each other that ignition, started at one point, would flash quickly to neighboring points exactly in effect as if it were a gaseous mixture. In such way most disastrous explosions have occurred in flour mills and starch factories, where the extremely fine dust of combustible starch, swept into the air by some accidental cause, and brought in contact with flame, has furnished the necessary conditions. The dust in coal mines also has caused explosion.

Explosive compounds.—Finally, there is still another and most inter- **568** esting type of explosive, in which the closest kind of contact is brought about. In these the combustible and the oxidizer are proximate constituents of one individual substance. In theoretical terms, they are parts of the same molecule instead of being in neighboring molecules. Therefore the explosive is a single substance and not a mixture. How this can be, is understood in recalling the fact that of potassium nitrate, $K_2O \cdot N_2O_5$, it is mainly the nitrogen oxide which supplies oxygen to the carbon in gunpowder. Now, if nitric acid could be combined in a salt with a combustible base—for example, one containing carbon and hydrogen—the condition of combustible and supporter of combustion would be realized in one compound, and it would only be necessary to break down the compound in order that the elements might recombine into carbon dioxide, water, and nitrogen. Such a base is found in common glycerine. which is only one of a numerous class of organic bases, called *alcohols*. The composition of glycerine is seen in the formula, $C_3H_5(OH)_3$, and its combination with nitric acid, after analogy with the formation of potassium nitrate, is shown by the equations:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O.$$
$$KOH + HNO_3 = K(NO_3) + H_2O.$$
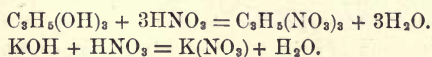
569 This glycerine trinitrate is more commonly known under the less correct name of *nitroglycerine*. The following equation shows that no outside oxygen is needed for the complete combustion :

$$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 6N + O.$$
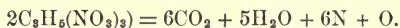
Nitroglycerine was discovered in 1847, but was practically unused until about 1863. Its successful application was due to a Swede, Nobel by name, who also discovered the method of firing by detonation. Nitroglycerine is made by adding glycerine, as a thin stream or spray, very slowly to a cooled mixture of sulphuric and nitric acids in the most concentrated form obtainable. It is important that all these substances be very pure and anhydrous. The temperature of the mixture must not rise above 30°; if it does, there is great danger. When the reaction is over, the nitroglycerine rises to the top and is drawn off, or the mixture is run into water in which the product sinks to the bottom as an insoluble oil. It must then be very thoroughly washed until free of acid, as the presence of this promotes decomposition and dangerous instability. It is sometimes strained through felt filters for additional purification.

570 Nitroglycerine is an oily, colorless, or nearly colorless liquid, heavier than water, with which it does not mix. It is somewhat volatile at 50° and freezes at about 8°, although the freezing point varies in different samples. It is poisonous, and is used as a powerful remedy in medicine. In the open air, small quantities may be burned without explosion, but when heated to about 180°, it explodes. It may also be exploded by a shock, either of a blow or by detonation. It is less sensitive in the frozen condition than in the liquid, and it is not commonly used in the latter form, except in order to "torpedo" gas and oil wells.

571 The volume of gas (counting the water as gaseous) from the explosion of one gram of nitroglycerine is about 714 cubic centimeters reckoned at 0°, and the temperature is about 3,000°. It is reckoned as from four to six times more effective than powder, at least in blasting rock. The velocity of detonation in the liquid is 5,300 feet per second. Owing to its properties, nitroglycerine does not need to be confined in order to be effective. Exploded on the surface of a rock, it may shatter the rock, for the action is so quick that the atmosphere is practically unyielding during the short interval.

572 In order to reduce the danger in handling liquid nitroglycerine, it is absorbed in some solid which in one class of explosives is inert, in another class the absorbent is itself explosive, or at least combustible. Of the first class, and the most common of all, is *dynamite*, which was invented by Nobel. The absorbent is a kind of clay made up largely of the silicious remains of minute organisms. This takes up about three

times its weight of nitroglycerine and forms a plastic mixture. The velocity of detonation in dynamite is 20,000 feet per second, four times that in the liquid, and its effective intensity is greater, but in smaller ratio; these facts are difficult of explanation. As absorbents, magnesia, powdered mica, sawdust, and charcoal are used to some extent.

Gun cotton is an explosive of the same chemical type as nitro- **573** glycerine. It is a nitrate of cellulose; cellulose is the alcoholic, organic base which constitutes the fundamental substance of the plant structure, and it is seen in nearly pure condition as cotton fiber and filter paper. The nitrate is made from thoroughly cleaned cotton by dipping it into the mixture of concentrated sulphuric and nitric acids. In this instance, also, it is very important that the acids be completely washed out, lest they provoke dangerous decomposition; therefore the cotton, which is hardly changed in appearance by nitrating, is reduced to pulp under water, then washed and pressed into compact forms as desired. When designed for military purposes, it is allowed to retain from 16 to 30 per cent of water, which renders it much safer, and does not interfere with its explosion by detonation. In this condition it is stored, for it is not sensitive to friction or percussion, nor to fire until the water is dried out of it. Even when dry it is not easily exploded by percussion, and it burns quietly if unconfined. When properly prepared, it is reckoned as "the safest explosive known." (Walke.)

The composition of gun cotton, reduced to the simplest terms, is **574** expressed by the formula $C_6H_7O_2(NO_3)_3$. The following equation shows that it does not contain enough oxygen for complete combustion:

$$2C_6H_7O_2(NO_3)_3 + 9O = 12CO_2 + 7H_2O + 6N.$$
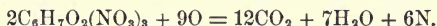
In the gaseous products of its explosion (there are no solids, hence no smoke) are found carbon monoxide and hydrogen, besides those in the preceding equation. The total volume of gas from one gram of gun cotton is given by one observer as 859 cubic centimeters, reckoned at 0°. This is more gas than either gunpowder or nitroglycerine gives, and the temperature produced is also higher than that of gunpowder. The velocity of detonation is greater in wet gun cotton than in dry, reaching about 20,000 feet per second, nearly four times the velocity in nitroglycerine and about the same as that in dynamite.

Gun cotton is used largely as a high explosive for military purposes, **575** in torpedoes, and in submarine mines. It is also used as a constituent in many other explosives. In some, additional oxygen is supplied by mixing with potassium or other nitrate. *Blasting gelatin* is a mixture of mono- and di-nitrocellulose and nitroglycerine, which contains some excess of oxygen. (See No. 569.) Nitrocellulose is also the chief

15

576 constituent of the smokeless powders which are displacing the black and the brown gunpowder for military and other uses. That which is prepared for the United States navy contains nitrocellulose mixed with barium nitrate, potassium nitrate, and calcium carbonate. *Cordite*, the powder adopted by Great Britain, contains nitroglycerine, nitrocellulose, and vaseline (Deering-Thorpe, F. H. Thorp, Walke).

17. CALCIUM

Ca.—39.7

577   *History.*—The preparation of lime, CaO, by the so-called burning of limestone, $CaCO_3$, and its use in making mortar, are of great antiquity. In 1756 Black showed the chemical relation between lime and limestone, and in 1808 Davy obtained the element as a metallic powder by the electrolysis of the chloride. Matthiessen, in 1856, also by electrolysis, succeeded in producing it as a coherent metal, and Moissan reinvestigated it in 1898.

578   **Natural occurrence.**—It is never found free. Its most abundant compound is the carbonate, which is known in its various conditions as limestone, chalk, marble, coral, calcspar, calcite, etc. The sulphate, $CaSO_4$, is also abundant under the names of *anhydrite* and gypsum. The phosphate, borate, silicate, and fluoride are native. Calcium salts are present in natural waters, and are essential to the plant organism, accumulating in the leaves, and also essential to the animal, occurring particularly in shells, bones, and teeth. The element is present in the sun, and has been found in meteorites.

579   **Preparation.**—Moissan prepared it (1898) by electrolyzing fused calcium iodide, CaI_2, at a dull-red heat, also by heating to dull red a mixture of the anhydrous iodide and sodium in a closed iron crucible.

The reaction is:

$$CaI_2 + 2Na = Ca + 2NaI.$$
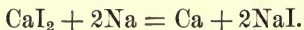
The iodide and the excess of sodium are dissolved out by anhydrous alcohol, which has been freed of dissolved air, and the calcium is left as a crystalline powder.

Properties (Moissan).—Calcium is a silver-white, crystal- **580**
lizable metal, soft enough to be cut with a knife. Its spe-
cific gravity is 1.85, and it melts at 760°. Heated in oxy-
gen to 300°, it burns brilliantly, with great evolution of
heat, forming the oxide CaO. Also in nitrogen it burns,
forming the crystallizable nitride Ca_3N_2. Both oxide and
nitride are formed when it burns in air. Heated in hydro-
gen, a crystalline hydride, CaH_2, is formed; and in chlorine,
the chloride, $CaCl_2$. It combines also directly with carbon
(CaC_2), with silicon, with sulphur, and with phosphorus
(Ca_3P_2). A compound with boron, and a second oxide,
CaO_2, are known. Calcium decomposes water on contact
at ordinary temperature, liberating hydrogen and forming
the oxide CaO, which combines with water and acts as
base in forming salts. The metal reduces the oxides of
lithium, sodium, and potassium, also carbon dioxide, when
heated with them, but not the oxide of magnesium. The
hydride, carbide, nitride, and phosphide decompose water
on contact by reactions, which are thus expressed:

$$CaH_2 + 2H_2O = CaO \cdot H_2O + 4H.$$
$$CaC_2 + 2H_2O = CaO \cdot H_2O + C_2H_2.$$
$$Ca_3N_2 + 6H_2O = 3CaO \cdot H_2O + 2NH_3.$$
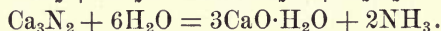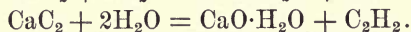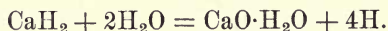
Lime, calcium monoxide, CaO, does not occur native. It **581**
is made on a large scale by heating the carbonate, $CaCO_3$;
the decomposition begins at about 400°. This is called
technically, but erroneously, "burning," and the product
"burnt" lime, or "quicklime." Lime is a white and, ordi-
narily, amorphous solid. Exposed to prolonged heating by
the oxyhydrogen flame, it slowly crystallizes at the surface,
but by the heat of the electric arc it fuses and volatilizes,
forming colorless, brilliant crystals. If impurities—e. g.,
alumina—are present, fusion takes place more readily, since
compounds with the lime are formed which are more fusi-
ble. The amorphous lime which is made from the carbon-
ate is hard and quite porous; by exposure to air it absorbs

water and carbon dioxide slowly, and falls into a soft powder, which is a mixture of hydroxide and carbonate. This makes quicklime a useful drying substance, especially for gases. On the other hand, if lime is brought in direct contact with a suitable quantity of water, combination takes place quickly with liberation of much heat; the hydroxide, $Ca(OH)_2$, is formed, and appears as a soft dry powder, if too much water is not present. This operation is called "slaking," and the product "slaked" lime. The heat of hydration may be sufficient to cause fire if combustible matter is present. The crystallized oxide, on contact with air or with water, changes very much more slowly than the amorphous, and apparently it does not dissolve until the combination with water has taken place.

582   **The hydroxide**, $Ca(OH)_2$, usually an amorphous powder, although crystallizable, is slightly soluble in water, 100 grams of the latter dissolving about 0.18 of a gram of the hydroxide at 20°, but only one half as much at 100°. The solubility, therefore, decreases with rise in temperature, which is exceptional. The solution has alkaline reaction and is often called "limewater." When more hydroxide is present than the water can dissolve, the mixture is called "milk of lime." The hydroxide loses its water at a red heat, the decomposition beginning even at 100° (Ramsay).

583   Lime finds a great variety of uses, for instances: in mortar and cements; in making glass, bleaching powder, and soda (by the Leblanc process); in purifying coal gas and sugar; in preparing many chemicals; in bleaching and dyeing cotton fabrics; in tanning leather; in obtaining metals from their ores; and as a disinfectant.

584   The monoxide and the hydroxide act as base and form a series of well known *salts*. The chloride, $CaCl_2$, when anhydrous is very deliquescent, and dissolves abundantly in water with evolution of heat. The crystallized chloride, $CaCl_2 \cdot 6H_2O$, dissolves with absorption of heat, and, mixed with ice or snow, may reduce the temperature to −40°; this

makes a convenient freezing mixture. Bleaching powder, and the carbonate, also the phosphate, have been sufficiently considered in other connections. The sulphide, CaS, in the impure form commonly made, is phosphorescent and used somewhat in making the luminous paints. The sulphate, $CaSO_4$, known as " plaster of Paris," is used in cements.

17a. *Mortar and other Cements*

Preparation of lime.—The primitive limekiln or furnace was a pit **585** sunken in the ground of a hillside; into it was piled the limestone in rather large lumps, leaving an opening and cavity at the bottom for the fuel. The hot gases and the carbon dioxide which is liberated are then free to pass upward through the loosely packed material and escape into the atmosphere. It is important that the carbon dioxide be thus swept away as produced, otherwise the carbonate may be reformed. Permanently constructed furnaces are now largely used. Excessive heating must be avoided, lest it cause the beginning of fusion, which gives a product that does not easily slake. This is more likely to happen with impure limestone. For other reasons also, approximate purity is desirable in many of the uses to which lime is put.

Mortar is a mixture of lime and sand which dries in the atmosphere **586** and hardens; it is used as a cement, as a covering for walls, and in many other ways. In its preparation, the quicklime is first slaked and mixed with water to a thin paste. If such a paste is allowed to dry, it shrinks considerably; therefore it is mixed with sand, and in this condition it is applied to brick or stone, so that it fills the separating spaces completely, and hardens to a compact mass without shrinkage. Sand, the grains of which are sharp and not rounded by friction, is preferred, as experience has shown that it makes a better mortar. After several days of exposure to air the mortar " sets "—that is, partly hardens. This is due to drying. After this change, a very slow absorption of carbon dioxide takes place, with the formation of carbonate, and this produces the second stage of hardening. The sand serves not only to increase the bulk of the lime, but also its porosity, and thus facilitates the absorption of carbon dioxide. If the drying is too quick or too complete, the hardening is interfered with, so that moisture plays an important part in the change; just how this is, and how the carbon dioxide penetrates to the interior, are not entirely clear. It is thought that the sand is not chemically changed in hardening, although in samples of mortar one hundred years old, or older, the silica, from 2

to 6 per cent of it, has been found in combination. The mortar in the Pyramid of Cheops, although older than 2000 b. c., is practically of the same composition as the modern mixture; and other mortars of Phœnician, Greek, and Roman masonry have been examined with similar result. In some instances the lime is found converted completely into carbonate, in others only partly so.

587 **Hydraulic lime.**—If limestone contains more than about 10 per cent of clay (aluminium silicate) when it is burned, it yields a lime which slakes less readily and with less heat, but which sets or hardens when in contact with water or even under water; hence it is called *hydraulic*. The hardening in this case is due to reaction between water and the anhydrous silicates and is independent of carbon dioxide. Such lime is of value in making *hydraulic mortar* or *cement* which is to be used in constructions with which water comes in contact. Certain natural anhydrous silicates of volcanic origin, when finely ground (without burning) and mixed with ordinary lime, constitute another variety of hydraulic cement; and blast-furnace slag, if cooled quickly from the melted condition, is similarly used with lime. Still a third variety is made by burning at a very high temperature an artificial mixture of pulverized calcium carbonate and clay. Of this variety is "Portland cement," which is made and also imported in large quantity in this country. The materials are ground and intimately mixed, then burned, and finally ground again. Much of the quality depends upon the proper heating. The setting and hardening are undoubtedly due to chemical reaction, but its exact nature is not easily explained. It is supposed that silicate and aluminate of calcium are formed by the heating, and that these combine with water and crystallize more or less, finally becoming as hard as natural stone.

588 **Plaster of Paris** is another variety of cement which finds many uses. This is made by heating to 120° or 130° the mineral, gypsum, which is a hydrated calcium sulphate, $CaSO_4 \cdot 2H_2O$. Only about three fourths of the water is thus expelled, so that plaster of Paris is chemically $(CaSO_4)_2 \cdot H_2O$. When this powder is mixed with water to a creamy paste, heat is liberated, the mixture swells somewhat, and quickly hardens to a white porous mass of smooth surface. If the gypsum is heated to 200°, all the water is driven off and the plaster does not set. The chemical changes of the hardening are explained as follows: The compound $(CaSO_4)_2 \cdot H_2O$ is somewhat soluble, and in solution slowly combines with water, thus:

$$(CaSO_4)_2H_2O + 3H_2O = 2(CaSO_4 \cdot 2H_2O).$$
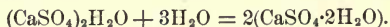
The latter hydrate, being less soluble than the first, separates in minute interlacing crystals. Plaster of Paris is used as a wall finish in the inte-

rior of buildings, also for making casts and reproductions for which the property of expanding in setting makes it especially applicable (Hartley-Thorpe and F. H. Thorp).

Review Problems

1. Assume that magnesium is converted into its iodide (see Exp. 41/b) by direct action, how much iodine is theoretically needed, and how much should the magnesium iodide weigh ? **588/1**

2. Suppose that one gram of magnesium is to be converted into magnesium pyrophosphate and as such weighed ; suggest the practicable operations for so doing, writing them out in the form of directions for the experiment, based on your knowledge of the properties of the substances involved and your experience in experimentation (see Exps. 446/₁ and 494).

3. Calculate what should be the weight of the pyrophosphate thus obtained.

4. Suppose that dry magnesium sulphate is to be the starting point for the same result as in 2, in what respect would you modify your directions ? What quantity of the sulphate should yield the same quantity of the pyrophosphate that one gram of magnesium yields ?

5. Does aluminium easily burn ? Suggest practicable steps by which one gram of aluminium may be converted into the oxide by converting first into the hydroxide. How much should the oxide thus obtained weigh ?

6. What is the ratio between those masses of magnesium and aluminium which exactly react with equal quantities of hydrochloric acid ? Also with equal quantities of oxygen ?

7. How much iodine should be needed exactly to convert sulphurous acid into sulphuric acid, making enough of the latter to neutralize exactly 39.8 grams of pure sodium hydroxide ?

8. Sulphuric acid may be completely precipitated from solution by adding sufficient barium chloride solution ; barium chloride in crystallized condition has the formula $BaCl_2 \cdot 2H_2O$: calculate how much of the latter would be necessary to precipitate exactly the sulphuric acid of 1 gram of sodium sulphate crystallized ($Na_2SO_4 \cdot 10H_2O$) ?

9. How much crystallized silver nitrate ($AgNO_3$) is necessary to precipitate exactly the chlorine of 1 gram of dry sodium chloride ?

10. What are the relative masses of chlorine and of anhydrous nitric acid (HNO_3) which are necessary to convert equal quantities of ferrous sulphate, $FeO \cdot SO_3$, into ferric sulphate, $Fe_2O_3 \cdot 3SO_3$? (See Nos. 532 and 317, Part I.)

11. As between sodium nitrate and potassium nitrate at the same

price per kilogram, which is the more economical material with which
to effect oxidation, other things being equal? What is the ratio of
economy?

12. As between magnesia and lime at the same price per pound,
which is the more economical material for liberating ammonia from
ammonium chloride? What is the ratio of economy?

G. General Survey

589   The general survey made of the first nine elements may
now be extended to include the seventeen. A study of the
fuller data of Table VII, No. 590, brings out in a striking
manner the peculiar progression in properties at first only
suggested. Thus as to *melting point*, beginning with so-
dium, and again with potassium, one sees a progression
like that which begins with lithium. The same may be
said as to the *combining volume*, as to the *heat of formation*,
the *valence*, and the *basic* and *acidic* function of the oxides.
Especially with regard to valence and the basic function is
clearly seen the tendency to recurring similarities at regu-
lar intervals or periods. Beginning with the alkali metal
lithium, valence increases by units to a maximum of four,
then decreases to one, and starting again at one with the
alkali metal sodium, it passes again through the same values
to reach one in the alkali metal, potassium. In the same
interval, the basic property diminishes, disappears, and re-
appears. This is the germ of what is known as *periodicity*.
Before giving a more detailed study to this important topic,
it is well to consider some facts descriptive of five addi-
tional elements which may be presented collectively.

TABLE VII

I.	II. Melting points. Boiling points.	III. Combining volumes.	IV. Oxides.	V.	VI. Formation heat of oxides.	VII. Chlorides.	VIII. Formation heat of chlorides.
H	B. P. $-238°$	Liquid, 14	H_2O	:	Liquid, 68,400 calories.	HCl	22,000 calories.
Li	M. P. $180°$	11.8	Li_2O	+	141,200	LiCl	93,800
Gl	M. P. $1,230°$	4.9	GlO	–	?	$GlCl_2$	?
B	Sublimes, $3,600°$ (?)	4.4	B_2O_3	+	317,200	BCl_3	104,000
C	Sublimes, $3,600°$ (?)	Diamond, 3.4	CO_2	–	97,000	CCl_4	21,000
N	B. P. $-194°$	?	N_2O_3	–	$-23,000$	NCl_3	$-38,100$
O	B. P. $-183°$	Liquid, 14.3	O_3	?	$-32,400$	OCl_2	$-17,800$
F	B. P. $-187°$	Liquid, 16.6	?	?	?	?	?
Na....	M. P. $96°$	23.2	Na_2O	+	100,400	NaCl	97,600
Mg..	M. P. $500°$–$600°$	13.8	MgO	+	143,400 (?)	$MgCl_2$	151,000
Al ..	M. P. $660°$	10.4	Al_2O_3	–	388,800	$AlCl_3$	161,000
Si ..	M. P. $1,100°$ (?)	11.2	SiO_2	+	219,000	$SiCl_4$	157,600
P ..	M. P. $44°$	Red, 14.4	P_2O_5(?)	–	370,000	PCl_3	75,500
S ...	M. P. $114°$	15.9	SO_2	–	71,000	SCl_2	?
Cl...	M. P. $-102°$	Liquid, 26.5	Cl_2O	–	$-17,800$	?	?
K....	M. P. $62°$	45.1	K_2O	+	98,200	KCl	104,300
Ca ..	M. P. $760°$	21.2	CaO	+	145,000	$CaCl_2$	169,800

21-25. CHROMIUM, MANGANESE, IRON, NICKEL,

Cr.—51.74.   Mn.—54.57.   Fe.—55.60.   Ni.—58.24.

COBALT

Co.—58.6

591   Following calcium in the list of elements are the three substances scandium, titanium, and vanadium, of which no detailed description is judged necessary in this limited course. Following these, still in the natural order, are five elements—chromium, manganese, iron, nickel, and cobalt. These bear so peculiar a relation to periodicity, and one in particular—namely, iron—so important a relation to every - day life, that some description of them is desirable.

592   *History.*—Chromium was first identified in its acid-forming oxide in 1797, but the element was separated much later. Manganese dioxide was known in very early years and used in making glass, but it was long confounded with the magnetic oxide of iron called loadstone, and the element was not obtained until 1774. Iron has been known from the earliest times; even the use of the metal is older than recorded history. An ore of nickel is mentioned as early as 1694. The impure metal was obtained in 1754. Cobalt in impure condition was described about 1735.

593   **Natural occurrence.**—None of these metals occurs native to any considerable extent. Free iron and nickel, with traces of cobalt, are found in meteorites. Chromium is neither abundant nor widely distributed. Manganese is not abundant but is widely distributed, occurring in many minerals often associated with iron, also to small extent in the soil and in plants and animals. Iron, on the other hand, is one of the most abundant and most widely distributed of the elements, as well as one of the most important in its relation to the industries. It is found in many minerals, also in the soil and in natural waters. It is an essential constituent of plants, being found with the green matter named chlorophyll; also of animals, constituting 0.2 per

cent of the red coloring matter of the blood. Iron is also present in the sun and many fixed stars. Nickel and cobalt are generally found together, but neither is very abundant or common. Both exist in the sun.

The chief ore of chromium is *chromite*, or chrome iron- **594** stone, $FeO \cdot Cr_2O_3$. Lead chromate, $PbCrO_4$, is found native, and emerald with some other green minerals owe their color to a small quantity of chromium which they contain. The most important ore of manganese is the dioxide, MnO_2, known as *pyrolusite*, also as the black oxide. Manganese is often found with iron. Iron occurs in great abundance as a sulphide, FeS_2, named iron *pyrites*, but this is not used as a source of iron. For this purpose the most important ores are the oxides. Among these are *hematite*, Fe_2O_3, or specular iron ore; *limonite*, the hydrated oxide, or brown hematite; and *magnetite*, or loadstone, Fe_3O_4. *Spathic* ore or *siderite* is the native carbonate, $FeCO_3$. Nickel occurs in combination with sulphur, also with arsenic, and as oxide and silicate. Cobalt in its most common ore is combined with sulphur and arsenic.

Preparation.—These elements are obtained in the metallic **595** condition, but not pure, through the removal of oxygen from their oxides by heating with carbon. Iron and nickel are thus commercially obtained, also alloys of iron with manganese and chromium. The elements are obtained in purer condition from the chlorides by electrolysis or by heating with magnesium, or in the cases of iron, nickel, and cobalt, by reducing their pure oxides with hydrogen. In nickel plating, the metal is deposited electrolytically. The commercial preparation of iron will be considered in a following section.

Properties.—These elements are all metallic, and in the **596** compact condition they are grayish-white, hard, and may be highly polished. Their melting points are high but not accurately enough determined to permit of satisfactory comparison. That of chromium is probably the highest of

the five, and manganese volatilizes at high temperature.
Some other data are given below:

597

NAME.	Sp. Gr. $(H_2O = 1)$	Comb. vol.	Formation heat of chlorides.	Solubility of chlorides in 100 of water.
Chromium	6.9	7.5	?	Very soluble.
Manganese	7.4	7.4	$MnCl_2 = 112,000$	62 at 10°
Iron......	8.1	6.9	$FeCl_2 = 82,100$	50 at 19°
Nickel....	about 9.0	6.5	$NiCl_2 = 74,500$	Slightly soluble at 100°
Cobalt....	about 9.0	6.5	$CoCl_2 = 76,500$	43 at 0°

Iron, nickel, and cobalt are attracted by the magnet, the
others not.

598   They burn in oxygen, and, except chromium, oxidize
in moist air and decompose water at high temperature,
but manganese oxidizes readily in the air and decomposes
water at ordinary temperature.   They combine directly
with the halogens, with boron, carbon, silicon, sulphur, and
phosphorus.   They dissolve in dilute hydrochloric acid,
chromium, and nickel with the least readiness.   None
shows a lower valence than two, and all form an oxide
of the type MO, and a hydroxide, $M(OH)_2$, which act
as bases; chromium monoxide, CrO, has not been sepa-
rated.   These hydroxides tend to take up more oxygen
but with decreasing readiness, which becomes almost zero
in nickel.   The following table shows the oxides of the
group:

599   (1) Chromium $CrO(?), Cr_2O_3, CrO_2, CrO_3,$ $CrO \cdot Cr_2O_3.$
      (2) Manganese $MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7, MnO \cdot Mn_2O_3.$
      (3) Iron $FeO, Fe_2O_3,$ $FeO_3(?)$ $FeO \cdot Fe_2O_3.$
      (4) Nickel $NiO, Ni_2O_3,$ $NiO \cdot Ni_2O_3.$
      (5) Cobalt $CoO, Co_2O_3,$ $CoO \cdot Co_2O_3.$

600   All the monoxides act as bases, and the corresponding
salts of chromium and iron tend to pass into salts of the
next higher oxide.   This property shows itself in less degree
with cobalt.

The oxides of the type M_2O_3, the so-called *sesquioxides*, **601** act as bases in forming salts, except that of nickel, in which the basic function is zero. It is only feeble in manganese and cobalt. At the same time the acidic function begins to appear in the chromium oxide, Cr_2O_3, for it dissolves in sodium and potassium hydroxides, but is reprecipitated on boiling. Possibly further evidence of acid function in the sesquioxides may be seen in the compounds $MgO \cdot Fe_2O_3$ and $ZnO \cdot Mn_2O_3$. It is doubtful if the dioxide, CrO_2, acts either **602** as base or acid, while MnO_2 seems to act very feebly in both capacities. The basic function entirely disappears in the trioxides, CrO_3, MnO_3, and FeO_3, which as acids form the **603** chromates, manganates, and ferrates. The trioxides lose a part of their oxygen with a readiness which increases from chromium to iron; so that the latter, FeO_3, has not been obtained free.

Of the still higher oxides, that of chromium, Cr_2O_7, has **604** not been obtained, and its existence even is doubtful. That of manganese, Mn_2O_7, acts only as acid, forming the *permanganates*, of which potassium permanganate is an example, $K_2O \cdot Mn_2O_7$. This also loses a part of its oxygen, as has been seen in the illustrative experiments involving its use.

The oxides of the type M_3O_4 are sometimes regarded as **605** made up of MO and M_2O_3 in combination. They are formed, that of iron for example, by heating the metal in air or oxygen. The scales which form on heating a bar of iron are this oxide. These oxides do not form distinctive salts.

All these metals show remarkable variation in properties **606** caused by the presence, even in small proportion, of impurities such as carbon, silicon, and phosphorus. As it is difficult to avoid their presence in the prepared metals, descriptions differ in many points. The influence of these substances on the properties of the metal has important bearing on the industrial use of the latter, which in the case of iron is very extensive.

23a. *Commercial Iron*

607   **The commercial forms** of this most important metal are usually grouped under three heads—cast iron, steel, and wrought iron. These differ very considerably, especially as to their physical properties, although chemically the difference is chiefly as to the proportion of *carbon* which they contain, As this, in part at least, is combined with the iron, evidently the difference in properties should not be regarded as due entirely to impurities, but to some extent as the difference of true compounds. At the same time there seems to be no sharply dividing line between the several varieties, and they pass gradually into each other. Wrought iron is the purest variety, containing generally less than 0.15 per cent of carbon. Cast iron contains from 1.5 to 6 per cent of carbon and is the most impure, while steel is between the two. In cast iron the carbon is partly combined with the iron as a carbide, and this, when the metal is dissolved in acid, forms a hydrocarbon with the hydrogen of the latter. The uncombined carbon appears then as graphite. The total carbon appears in the latter condition, when the metal is dissolved by a copper salt. (Compare Exp. 17/4 and note.) Two subvarieties of cast iron are recognized, the *white* and the *gray*. In the former the combined carbon predominates, in the latter the graphite. The gray variety is softer and melts at a higher temperature, but is better for casting than the white because more fluid. Slow cooling favors the production of the gray, rapid cooling of the white, perhaps because the carbides, formed at the high temperature, tend to decompose on cooling.

608   *Silicon* is also an impurity of cast iron, averaging from 1 to 4 per cent. In these proportions it tends to make the metal soft and strong and suitable for casting, but in larger proportion it renders it hard and brittle. High temperature and silicious "slags" in the process of manufacture tend to increase the quantity of silicon in the product.

609 ·   *Sulphur* is an objectionable impurity, which is present only in small quantity—a few hundredths of 1 per cent in good cast iron. High temperature in making, and the presence of silicon or manganese in the metal and of lime in the slag, tend to eliminate the sulphur.

Manganese is always present in cast iron. With 20 per cent or more the product is known as ferro-manganese. Its presence is generally advantageous.

610   *Phosphorus* has a bad effect in making steel and wrought iron brittle.

The following table gives, for illustration, the composition of samples of cast iron, steel, and wrought iron :

CONSTITUENTS.	Gray cast iron.	White cast iron.	Besse-mer soft steel.	Siemens soft steel	Hard steel.	Cruci-ble steel.	Wrought iron.
Graphitic carbon	2.65	0.20					
Combined "	0.08	2.00	0.126	0.167	1.144	0.36	0.06
Silicon.........	2.95	0.71	0.135	0.023	0.166	0.02	0.04
Manganese.....	0.40	0.50	0.158	0.044	0.104	0.30	0.08
Phosphorus	1.84	0.47	0.06	0.062	.....	0.03	0.20
Sulphur	0.06	0.19	0.014	0.013	.....	0.02	0.05
Iron	92.02	95.93					

The *melting point* of wrought iron is given as varying from 1,900° to 2,100°, of steel from 1,300° to 1,400°, and of cast iron from 1,100° to 1,200°.

The manufacture.—The ores commonly used in making iron are the **611** oxides or carbonates. In some instances these undergo a preliminary heating or *calcination*, for the purpose mainly of converting the ferrous compounds into the ferric, and of making the material more porous.

The ore is reduced in the *blast furnace*. This is an upright shaft, like a large chimney, but considerably narrower at the top and bottom than at the middle, so that the upper and lower thirds of its height are conical instead of cylindrical. This is lined with fire-brick, the outside being built of iron plates. The charge is introduced at the top and consists of the ore with alternate layers of coke and limestone. The blast of air, under a pressure varying from four to ten pounds per square inch and at a temperature of 200° to 400°, is forced in at the base. The following figures give an approximation of the relative quantities employed:

Charge.	Cwt.	Products.	Cwt.
Calcined ore...........	48	Iron	20
Limestone	12	Slag	30
Coke...................	20	Waste gases	130
Blast	100		180
	180		

The *chemical reactions* are complicated. Their general character **612** may be thus described: The fuel is converted into carbon dioxide and monoxide. The ore in the first part of its descent is rapidly heated to low redness. At this temperature the monoxide, which constitutes 36 per cent of the gases at this portion of the furnace, acts on ferric oxide thus:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$
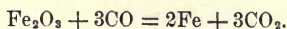
The iron is in the form of metallic sponge, the temperature not being high enough to melt it. Below the region of this reaction the lime-

stone is decomposed, and the dioxide which is produced aids in protecting the iron from reoxidation.   As the material settles in the furnace the temperature increases, and carbon is formed by the reduction of the monoxide and is deposited in the porous, spongy iron in a manner favorable to combination with the latter.   This takes place when the suitable temperature is reached, and as a consequence the product becomes fusible in the existing conditions; the molten metal accumulates in the lowest part of the furnace, called the " hearth " or " crucible."   The silica combines with the lime, and alumina if present, of the charge and makes the fusible slag which floats on the heavier molten metal.   The latter is drawn off at suitable intervals and run into rough molds.   In this form it is known as " pig iron."

613   From this cast iron both *wrought iron* and *steel*, the former first, are made by processes of refining.   These consist chiefly in burning out the carbon.   In an older method, now little used, this is accomplished by melting the cast iron on a hearth and directing upon it a blast of air.   The carbon burns away to the monoxide, the silica combines with ferrous oxide, also formed, and produces a slag which protects the iron from further oxidation.   This, in consequence of losing carbon, has a higher melting point and becomes pasty.   The semi-fused mass, called the " bloom," is removed from the furnace and freed of the slag by beating under the steam hammer.

614   A modification of this process, known as *puddling*, was introduced in 1784, and further modified about 1820.   The cast iron is heated by the furnace flame on a hearth made of iron " scales " (oxide).   The carbon is burned by the oxygen of the iron oxide, and, as the metal melts and finally becomes pasty, it is stirred mechanically or " puddled."   The " blooms " are hammered, as before.

615   A third method is that of *Bessemer*, which has revolutionized the steel industry.   It was patented in 1856.   In this the iron, which should contain not more than a few hundredths per cent of phosphorus nor more than 2 or 3 per cent of silicon, is turned in molten condition from the blast furnace into an egg-shaped vessel, called the " converter," which has been previously heated.   This is so supported that it can be inverted, like a huge pitcher.   It is fitted with a movable false bottom, and is lined with some silicious material.   While the converter is in horizontal position it is charged with molten cast iron. weighing from five to ten tons.   A blast of air under the pressure of about 20 pounds to the square inch is then blown through the false bottom, and, the vessel having been restored to the vertical position, the air is forced through the melted metal.   By this means the silicon is burned to the dioxide and passes into

the slag. The carbon is next burned, and the flame of the monoxide appears above the metal until the carbon is all eliminated. The temperature is sufficient to keep the metal in liquid condition, and it may be thus drawn off into molds. In this degree of purity, however, it is too soft for many purposes, so carbon is added by putting into the converter after the refining is finished, but before the metal is poured, the necessary quantity of iron containing a known amount of carbon, and often also some manganese. By this means steel is produced which contains the desired proportion of carbon. By this Bessemer process the sulphur and phosphorus are not removed, but remain combined with the iron; hence the need that the original cast iron shall not contain these impurities in objectionable proportion.

616 In the *basic Bessemer* process the lining of the converter is made of lime and magnesia instead of the acidic silicious material, and lime is added to the charge. By this modification iron containing phosphorus may be used, since the latter is converted in the presence of these bases into phosphates, and the sulphur into sulphates, which pass into the slag; but it is important that the iron be low in silicon. This phosphoric slag is used as a source of phosphates. (See No. 502, Part I.)

617 In the *Siemens-Martin* process, by improved methods of heating, cast iron is melted on a hearth and decarbonized by adding the suitable quantity of wrought iron or steel scrap, and the product is still kept in fused condition. This is also known as the "open-hearth" process, and is operated in both the acidic and basic modifications. It has the advantage over the Bessemer of more easy control.

618 Another variety of steel is made by the *cementation* process. Wrought-iron bars are placed in fire-clay boxes, packed with charcoal, and kept at red heat for several days. In some manner not well understood the carbon is absorbed and steel produced, which is forged under the hammer.

619 Steel, when quickly cooled after heating to a high temperature, is made harder; if the temperature is very high, the steel is also brittle, but if somewhat lower it is left elastic. If the cooling is slow, it is softer and tougher. These changes are technically called *hardening*, *tempering*, and *annealing* (Turner-Thorpe and Ramsay).

H. The Law of Periodicity

620 The details of description through which we have passed have, no doubt, seemed to you tedious at times, but

16

if by this presentation you have been brought not only into acquaintance with a considerable number of substances, all of scientific and many of practical importance, but in addition shall have been brought to a fair appreciation of the significance of the great law of periodicity, no student of you should grudge the time and labor; for, if the writer be not wrong, this may justly be reckoned one of the most beautiful and significant generalizations to be found in the scientific study of nature. It seems so simple and so evident in the facts set forth, that one wonders it should not have been earlier discovered; there will be interest, therefore, in considering very briefly some of the ideas which preceded the discovery.

621   **Classification.**—Early in the development of chemistry attempts were made to classify the elementary substances according to similarities into groups or families, the members of which should possess certain properties in common; just as in other branches of natural science, plants and animals are classified by their resemblances. As illustration are cited some of the families suggested by Dumas, an eminent French scientist (1828). Separating the elements first into *metals* and *non-metals*, he divided the latter into five families:

1st.	2d.	3d.	4th.	5th.
Hydrogen.	Fluorine.	Selenium.	Nitrogen.	Boron.
	Chlorine.	Sulphur.	Phosphorus.	Silicon.
	Bromine.	Oxygen.	Arsenic.	Carbon.
	Iodine.			

Similar groups among the metals were made, for example:

Lithium.	Calcium.
Potassium.	Strontium.
Sodium.	Barium.
	Lead.

Now, all classification of this kind implies the selection **622** of some few properties, the common possession of which shall constitute the basis for the grouping. This selection is arbitrary, and the determination of how many and what properties shall be chosen is generally influenced by notions of the relative importance of this or that property or resemblance. Thus it comes about that when attempt is made to put objects of nature in groups thus constituted, difficulty is very frequently met, for individuals are found which do not fit into the groups—individuals which may perhaps be placed equally well in one as in another group, or perhaps may not be satisfactorily placed in any. Nevertheless, classification of this kind, although imperfect, is of practical use, but an important advance upon this is gained in recognizing that differences as well as resemblances must be taken into account.

Numerical relations.—Early attempts were made also to **623** trace simple numerical relations between similar elements. In this connection Dumas (1857) may be again mentioned, and also Professor Cooke, of Harvard University (1854). For example, the following relations were pointed out:

	O	S	Se	Te
$a = 16$	16	32	80 (79)	128 (127)
$d = 8$	a	$a + 2d$	$a + 8d$	$a + 14d$

	Li	Na	K	
$a = 7$	7	23	39	
$d = 8$	a	$a + 2d$	$a + 4d$	

	Mg	Ca	Sr	Ba
$a = 24$	24	40	88 (87.5)	136 (137)
$d = 8$	a	$a + 2d$	$a + 8d$	$a + 14d$

Prout's hypothesis.—As early as 1815 Prout suggested **624** that the numbers at that time assigned as combining weights were whole numbers or approximated whole numbers, and therefore that the elements might be themselves built up from some one elemental substance, probably hydrogen. This led to much speculation, and finally to rede-

terminations of the combining weights. To the work of Stas (1860–'65) in this matter reference has elsewhere been made (see No. 145). His results reached the highest degree of accuracy up to that time attained, and still remain unsurpassed. The outcome proved that the combining weights in many instances could not be reckoned as whole numbers. Dumas then argued that they were exact multiples of one half. But clearly, if speculation is to go to this extent, the exact combining weights need be no obstacle, for by choosing a basal quantity sufficiently small any set of numbers may be reckoned as exact multiples of the former. This conception that the elements may have been derived from some single primitive substance is known as the *unitary theory of matter*, and it still receives more or less attention.

625   **Periodicity.**—The arrangement of the elements in the order of increasing combining weights was first proposed in 1853 by Gladstone, an English chemist, but there was much inaccuracy in the values of that day, and he failed to discover what was later revealed by a similar arrangement. The first clear recognition and formulation of the law of periodicity is generally credited to Mendeléeff, a Russian, and to Lothar Meyer, a German, who published their views at nearly the same time (1869) and independently of each other. The name of the former is more commonly associated with the law. After the law as announced by them had received very general attention, it was discovered that in 1864 an Englishman named Newlands had published a paper in which, under the name of " The Law of Octaves," he seemed to have recognized in a measure the phenomenon which was later and better named periodicity. Newlands's work, however, received but little attention at the time.

626   The law may be thus formulated : *The elements being arranged in the order of increasing combining weights, their properties vary from element to element, but tend to return*
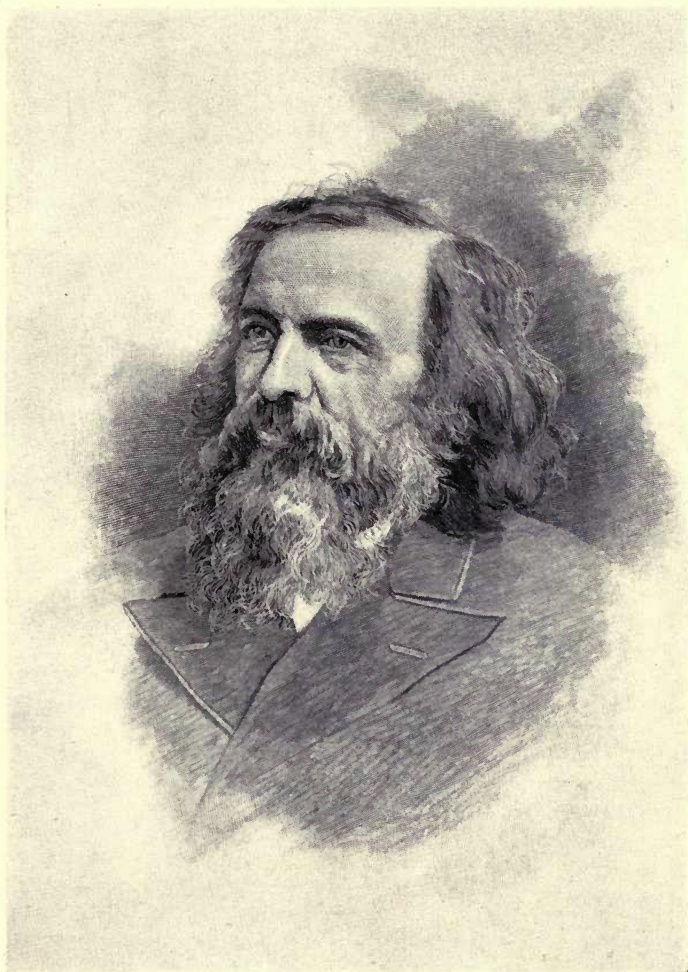
DIMITRI IVANOVITCH MENDELÉEFF

B. Siberia, 1834.

(See Nos. 625, 638, 639, 641.)

to similarity at regular intervals or periods. This is expressed more technically as follows : *The properties of the* **626/1** *elements are periodic functions of their combining weights.* The groupings brought about under the law are conveniently set forth in tabular form, as seen in Table VIII, on the following page.

The Elements by Periods

Thus tabulated, the similar elements fall into the ver- **628** tical columns, usually designated as *groups* or families, and the horizontal rows constitute the periods. (Hydrogen is not included in the table. It may be looked upon as the sole representative of one period.) The periodic variation of properties becomes clearly evident in the first and second periods. It is to be particularly noted that the change from extreme acidic to extreme basic function is abrupt in passing from fluorine to sodium, and that the valence is unchanged. The same is true in passing from chlorine to potassium. In the third period the placing of manganese in the sixth group is one of the unsatisfactory and puzzling features of the scheme, for it is rather difficult to find any close relationship between it and chlorine and fluorine. It is distinctly metallic and the lower oxide, MnO, acts as base, while the oxides, Mn_2O_6 and Mn_2O_7, act as acids. It seems never to act as a monad. Between manganese and copper, which is placed in Group I, are three metals—iron, nickel, and cobalt—whose combining weights are close together, and whose properties are very similar. They act almost exclusively as bases, and they show no valence less than two. Then follows copper, which acts only as a base and has a valence, in some compounds, of one, like the alkalies, and in others a valence of two, like the iron, nickel, and cobalt. These three elements, therefore, make the change gradual from Group VII to Group I, and they constitute what is called a *transition* group.

TABLE VIII.—Law of Periodicity

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1.	6.97 Li LiCl +	9 Gl GlCl$_2$ + −	10.9 B BCl$_3$ − +	11.9 C CCl$_4$ −	13.9 N NCl$_3$ or H$_3$ −	15.88 O OCl$_2$ −	18.9 F HF −	
2.	22.9 Na NaCl +	24.1 Mg MgCl$_2$ +	26.9 Al AlCl$_3$ + −	28.2 Si SiCl$_4$ −	30.8 P PCl$_3$-Cl$_5$ −	31.8 S SCl$_2$ SCl$_4$ −	35.2 Cl HCl −	
3.	38.8 K KCl +	39.7 Ca CaCl$_2$ +	43.8 Sc ScCl$_3$ +	47.8 Ti TiCl$_4$,Cl$_{2-3}$ − +	51 V VCl$_{3-2-4}$	51.7 Cr CrCl$_2$, Cl$_3$ − +	54.6 Mn MnCl$_{2-3-4}$ − +	Fe 55.6 FeCl$_2$ FeCl$_3$ + − / Ni 58.2 NiCl$_2$ + / Co 58.6 CoCl$_2$ CoCl$_3$ +
4.	63.1 Cu CuCl CuCl$_2$ +	64.9 Zn ZnCl$_2$ + −	69.4 Ga GaCl$_3$ GaCl$_2$ + −	71.9 Ge GeCl$_4$ − +	74.4 As AsCl$_{3-5}$ − +	78.5 Se H$_2$Se SeCl$_4$	79.3 Br HBr −	
5.	84.8 Rb RbCl +	87 Sr SrCl$_2$ +	88.3 Y YCl$_3$ +	89.7 Zr ZrCl$_4$ − + ZrH$_2$ −	93 Cb CbCl$_{3-5}$ −	95.3 Mo MoCl$_{2-3-4}$ − +	0	Ru 100.9 RuCl$_2$ RuCl$_3$ + − / Rh 102.2 RhCl$_3$ + / Pd 105.6 PdCl$_2$ PdCl$_4$ +
6.	107 Ag AgCl +	111.4 Cd CdCl$_2$ +(−?)	113 In InCl$_{1-2-3}$ + −	118 Sn SnCl$_{2-4}$ + −	119 Sb SbCl$_{3-5}$ + −	(?) 126.5 Te TeCl$_{2-4}$ −	125.9 I HI −	
7.	131.9 Cs CsCl +	136.4 Ba BaCl$_2$ +	137.5 La LaCl$_3$ +	139 Ce CeCl$_3$-($_4$?) +(−?)	0	0	0	0 0 0
8. 9.	0	0	0	0	181.6 Ta TaCl$_{3-5}$ −	183 W WCl$_{2-4-5-6}$ −	0	Os 189.6 OsCl$_{2-3-4}$ + − / Ir 191.6 IrCl$_{3-4}$ + / Pt 193.3 PtCl$_{2-4}$ −
10.	195.7 Au AuCl$_{1-2}$(?)$_{-3}$ + −	198.5 Hg HgCl$_{1-2}$ +	202.6 Te TeCl$_{1-2-3}$ + −	205.3 Pb PbCl$_{2-4}$ + −	206.5 Bi BiCl$_{3-5}$ +(−?)			

From bromine, Group VII, period 4, which is very simi- **629** lar to chlorine, the change is again abrupt to rubidium, period 5, which greatly resembles potassium. On the other hand, the passage from period 5 to period 6 is through the transition group of three elements, but the representative of the seventh group in this period is lacking. From period 6 to period 7 the change from iodine to cæsium is abrupt. The last portion of period 7, the whole of period 8, and the first portion of period 9 are lacking, although possibly some of the rare elements (Nos. 53–60, Table XI, No. 644) which are not yet sufficiently well known may later fill some of the vacant places.

The Elements by Groups

The consideration of the groups brings out some addi- **630** tional features. Thus in Group I, after the second period, the resemblance between potassium, K, rubidium, Rb, and cæsium, Cs, is much more marked than between these and copper, Cu, silver, Ag, and gold, Au. The former three are also more like sodium and lithium than are the latter three. The former are set off to the left and the latter to the right of the column. It is notable that they alternate. The same plan is followed in all the other groups, but the divergence in properties between the left-hand and right-hand series is especially marked in Groups I, II, VI, and VII.

Several instances may be noted of approximately equal differences between successive combining weights in the vertical columns. (See also No. 623.)

The comparison of properties in vertical columns, as **631** before was done in the horizontal rows, shows the progression of properties also in this direction. Some such numerical values for Groups I and II are tabulated on the following page, in order to make the relation quickly evident to the eye :

Table IX

632

Melting Points

I		II	
Li 180°		Gl 1,230°	
Na 96°		Mg 500°–600°	
K 62°	Cu 1,330° (?)	Ca 760°	Zn 420°
Rb 39°	Ag 1,040°	Sr ?	Cd 320°
Cs 27°	Au 1,240°	Ba ?	Hg −39°

633

Combining Volumes

I		II	
11.8		4.9	
23.2		13.8	
45.1	7.1	21.2	9
56.5	10.1	34.8	13
70.2	10.1	37	14.6

634

Formation Heat of Oxides

I		II	
141,200		?	
100,400		143,400 (?)	
98,200	40,800	145,000	85,800
?	5,900	128,400	66,400 (?)
?	?	124,200	20,700

635

Formation Heat of Chlorides

I		II	
93,800		?	
97,600		151,000	
104,300	32,850	169,800	97,200
?	29,400	184,600	93,200
?	5,800	194,700	53,200

636

Solubility of Chlorides

I		II	
63.7 (0°)		Very sol.	
35.7 (1°)		52.2 (0°)	
28.7 (1°)	Insol.	50 (0°)	300 (19°)
76.4 (1°)	Insol.	44.5 (1°)	143 (20°)
?	Insol.	31.2 (1°)	7.39 (20°)

The law of means.—It is evident from data of the kind **637**
cited that each element tends to be intermediate in its
properties between the element which precedes it and that
which follows it, both in the periods and in the groups.

Mendeléeff's predictions.—At the time that Mendeléeff **638**
published his table, based on the law of periodicity, there
was no element in the list between calcium, II 3, and tita-
nium, IV 3. He saw clearly that the latter should be placed
in Group IV, from its resemblance to silicon and carbon.
He therefore left the space III 3 unoccupied. Also be-
tween zinc, II 4, and arsenic, which evidently belonged in
V 4, no element was known. He therefore left two blank
spaces at these points. But, more than this, confident in
the fundamental truth of the law which he had announced,
he affirmed the probable existence of elements with prop-
erties which would fit them in these vacant spaces, and
he predicted their ultimate discovery. Furthermore, he
predicted with considerable definiteness their properties
in several respects, including combining weight, valence,
melting point, solubility, basic and acidic function, etc.
In 1875 a new element was discovered by Lecoq de Bois-
baudran, a Frenchman, and named by him *gallium*, in honor
of his country. Its properties were found to agree almost
item for item with those predicted by Mendeléeff for the
unknown element, III 4. In 1879 another new element
was discovered by Nilson and named *scandium*, in honor of
Scandinavia. This was found to be Mendeléeff's unknown
element III 3, agreeing closely with the predicted proper-
ties. In 1886 a third remarkable verification of the law
was made in the discovery, by Winkler, of an element which
he named *germanium*, and which corresponds closely with
the element predicted for IV 4. Thus in three separate
instances has discovery justified in the most striking man-
ner the faith of Mendeléeff, that he had formulated a great
and fundamental truth of nature. And it is interesting
to note the three nationalities which, in the commemorative

names of the three elements, bear witness to the brilliant discovery of a Russian. An analogous discovery in astronomy affords an interesting comparison. Based upon observed peculiarities in the motion of the outermost planet of the solar system as known at that time—namely, the planet Uranus—the French astronomer, Leverrier, and an Englishman, Adams, concluded that there must be a planet outside of Uranus, and they calculated its probable position at a specified time. Their surmise and calculations were verified shortly afterward by the discovery, in 1846, of the planet Neptune by Galle, of Berlin, in the position indicated by the calculations.

639 Mendeléeff at a more recent date (1889) has said : " I foresee some more new elements, but not with the same certitude as before," and he describes a possible element for the place, VI 10 (Principles of Chemistry, vol. ii, p. 447). Much interest, too, would attach to an element for the place, VII 5. Naturally the discovery of a new element at once suggests the question, Where will it fit in Mendeléeff's scheme ? And so, concerning the more recently discovered elements, argon, helium, and neon, there is much discussion with reference to this matter without as yet, it must be said, any satisfactory conclusion.

640 **Applications of periodicity.**—The notion of periodicity once established, it is applicable in determining the combining weight from the experimentally determined equivalent weight. Thus in the instance of glucinum the relation of periodicity was urged in favor of the combining weight, 9, the second multiple instead of 13.5, the third multiple, before the determination of the specific gravity of the gaseous chloride confirmed the choice of the former. There is still question as to the exact combining weight of tellurium, VI 6. Its periodic relation should make the value less than that of iodine, while recent determinations show a slightly higher value, and it is doubted if the substance in hand is truly elemental. There is a similar ques-

tion as to the relative order of nickel and cobalt, VIII 3. Again, new and more accurate determinations of the combining weights established the periodic order of osmium, iridium, platinum, and gold, as given in the table, whereas the earlier order was gold, iridium, platinum, and osmium.

Conclusion.—Finally, although there are still unsatisfac- **641** tory features of the Mendeléeff table when it is attempted to include all the elements, particularly among those of high combining weight and those of which little is now known, and although the law is still incompletely and imperfectly expressed, it may nevertheless be fairly claimed in its behalf that it is a discovery of the very highest order. This claim is justified by the broad significance of the underlying principle, by its usefulness in testing the validity of conclusions, by its revealing otherwise unrecognized relations, and by its fertility of suggestion. As Mendeléeff says, a true law of nature leads to improved methods of research, anticipates facts, foretells magnitudes, gives a hold on nature (Principles of Chemistry, vol. ii, p. 26).

AFTERWORD

642　THE starting point of this brief course was the simple observation that the things about us are not permanent but changeful. In your developing experience you have seen these changes grow bewilderingly numerous and varied. Then, deepening penetration has shown all their complexity resolved into the simpler changes—namely, the combinations and recombinations of the elemental forms of matter. Looking still further into the nature of these changes, you have seen that they are subject to simple laws of quantity, as a consequence of which they manifest themselves always associated in a peculiar manner with certain definite masses of matter. Next, one phenomenon after another, seemingly of most diverse nature, has been brought into close relation with these same definite masses. The following step extended the range of your experience and brought you to a closer acquaintance with a few of the innumerable and varied kinds of matter. And, finally, these, in spite of their multiplicity and variety, are brought into orderly relation with the same definite masses. And thus that which otherwise would be chaotic and meaningless reveals itself to you as the order and symmetry of intelligence manifest in things. What you have seen and heard is but a fragment ; vastly more remains untold and yet more undiscovered.

But, now at the end of the course, if you have come to realize somewhat better than before the beauty and signifi-cance of the physical world in which you live, and have been brought into closer touch with the great nature of which you form a part, then you have gained something of worth which will stay by you long after the single facts and experiences which were its accompaniment shall have passed from your minds.

643   TABLE X.—*The Elements in Alphabetical Order*

No.	NAME.	Symbol.	Combining weight. H=1.	Combining weight. O=16.
11	Aluminium	Al	26.9	27.1
46	Antimony...............	Sb	119.1	120.0
74	Argon	A	19.8	
30	Arsenic	As	74.4	75.0
50	Barium	Ba	136.39	137.4
70	Bismuth	Bi	206.5	208.1
4	Boron	B	10.86	10.95
32	Bromine	Br	79.35	79.96
43	Cadmium...............	Cd	111.4	112.2
49	Cæsium	Cs	131.9	132.9
17	Calcium	Ca	39.7	40.0
5	Carbon	C	11.91	12.0
52	Cerium	Ce	139.0	140.0
15	Chlorine	Cl	35.18	35.45
21	Chromium	Cr	51.74	52.14
25	Cobalt.................	Co	58.6	59.0
37	Columbium or niobium...	Cb	93.0	94.0
26	Copper	Cu	63.12	63.60
58	Erbium	Er	164.7	166.
8	Fluorine	F	18.91	19.06
56	Gadolinium	Gd	155.6	156.8
28	Gallium	Ga	69.4	70.0
29	Germanium	Ge	71.9	72.5
3	Glucinum or beryllium ...	Gl	9.0	9.1
66	Gold...................	Au	195.7	197.2
73	Helium	He	1.98	
1	Hydrogen...............	H	1.	1.008
44	Indium	In	113.0	113.9
47	Iodine	I	125.89	126.85
64	Iridium................	Ir	191.6	193.0
23	Iron	Fe	55.6	56.0
51	Lanthanum	La	137.45	138.5
69	Lead	Pb	205.34	206.9
2	Lithium	Li	6.97	7.03
10	Magnesium	Mg	24.10	24.28
22	Manganese	Mn	54.57	55.0
67	Mercury	Hg	198.5	200.0

TABLE X.—*The Elements in Alphabetical Order* (*continued*)

No.	NAME.	Symbol.	Combining weight. H=1.	Combining weight. O=16.
38	Molybdenum	Mo	95.3	96.0
54	Neodymium	Nd	142.5 (?)	143.6 (?)
75	Neon	...	9.5	
24	Nickel	Ni	58.24	58.7
6	Nitrogen	N	13.93	14.04
63	Osmium	Os	189.6	191.0
7	Oxygen	O	15.88	16.00
41	Palladium	Pd	105.6	106.4
13	Phosphorus	P	30.8	31.0
65	Platinum	Pt	193.3	194.8
16	Potassium	K	38.82	39.11
53	Praseodymium	Pr	139.4 (?)	140.5 (?)
40	Rhodium	Rh	102.2	103.0
33	Rubidium	Rb	84.78	85.43
39	Ruthenium	Ru	100.9	101.7
55	Samarium	Sm	149. (?)	150. (?)
18	Scandium	Sc	43.8	44.1
31	Selenium	Se	78.5	79.1
12	Silicon	Si	28.2	28.4
42	Silver	Ag	107.11	107.92
9	Sodium	Na	22.88	23.05
34	Strontium	Sr	86.95	87.6
14	Sulphur	S	31.83	32.07
61	Tantalum	Ta	181.6	183.1
48	Tellurium	Te	126.5	127.5
57	Terbium	Tb	158.8 (?)	160. (?)
68	Thallium	Tl	202.6	204.1
71	Thorium	Th	230.8	232.6
59	Thulium	Tu	169.4 (?)	170.7 (?)
45	Tin	Sn	118.1	119.0
19	Titanium	Ti	47.8	48.1
62	Tungsten	W	183.	184.4
72	Uranium	U	237.8	239.6
20	Vanadium	V	51.0	51.4
60	Ytterbium	Yt	171.7	173.
35	Yttrium	Y	88.3	89.0
27	Zinc	Zn	64.9	65.4
36	Zirconium	Zr	89.7	90.4

TABLE XI.—*The Elements in Natural Order*

No.	NAME.	Symbol.	Equivalent weight.	Fac-tor.	Combining weight.* H = 1.	Combin-ing wt.* O = 16.
1	Hydrogen........	H	1.	1	1.	1.008
2	Lithium	Li	6.97	1	6.97	7.03
3	Glucinum or beryllium	Gl	4.5	2	9.0	9.1
4	Boron	B	3.62	3	10.86	10.95
5	Carbon	C	2.9775	4	11.91	12.00
6	Nitrogen.......	N	4.643	3	13.93	14.04
7	Oxygen........	Ö	7.94	2	15.88	16.00
8	Fluorine	F	18.91	1	18.91	19.06
9	Sodium	Na	22.88	1	22.88	23.05
10	Magnesium	Mg	12.05	2	24.10	24.28
11	Aluminium	Al	8.967	3	26.9	27.1
12	Silicon........	Si	7.05	4	28.2	28.4
13	Phosphorus	P	10.267	3	30.8	31.0
14	Sulphur	S	15.91	2	31.83	32.07
15	Chlorine	Cl	35.18	1	35.18	35.45
16	Potassium	K	38.82	1	38.82	39.11
17	Calcium	Ca	19.9	2	39.7	40.0
18	Scandium......	Sc	14.6	3	43.8	44.1
19	Titanium	Ti	11.95	4	47.8	48.1
20	Vanadium	V	17.0	3	51.0	51.4
21	Chromium	Cr	17.25	3	51.74	52.14
22	Manganese.....	Mn	27.28	2	54.57	55.0
23	Iron...........	Fe	27.80	2	55.6	56.0
24	Nickel.........	Ni	29.12	2	58.24	58.7
25	Cobalt.........	Co	29.3	2	58.6	59.0
26	Copper	Cu	31.56	2	63.12	63.60
27	Zinc...........	Zn	32.45	2	64.9	65.4
28	Gallium	Ga	23.13	3	69.4	70.0
29	Germanium	Ge	17.975	4	71.9	72.5
30	Arsenic.......	As	24.8	3	74.4	75.0
31	Selenium	Se	39.2	2	78.5	79.1
32	Bromine	Br	79.35	1	79.35	79.96
33	Rubidium......	Rb	84.78	1	84.78	85.43
34	Strontium	Sr	43.47	·2	86.95	87.6
35	Yttrium	Y	29.4	3	88.3	89.0
36	Zirconium	Zr	22.43	4	89.7	90.4

* According to Clarke, Journal of the American Chemical Society, xxi, 213, February, 1899; and Richards, American Chemical Journal, xx, 543 (July, 1898).

TABLE XI.—*The Elements in Natural Order* (*continued*)

No.	NAME.	Symbol.	Equivalent weight.	Fac- tor.	Combining weight. H = 1.	Combin- ing wt. O = 16.
37	Columbium or niobium	Cb	31.	3	93.	94.0
38	Molybdenum ...	Mo	47.6	2	95.3	96.0
39	Ruthenium	Ru	50.45	2	100.9	101.7
40	Rhodium	Rh	51.1	2	102.2	103.0
41	Palladium	Pd	52.8	2	105.6	106.4
42	Silver	Ag	107.11	1	107.11	107.92
43	Cadmium	Cd	55.7	2	111.4	112.2
44	Indium	In	37.67	3	113.0	113.9
45	Tin	Sn	29.5	4	118.1	119.0
46	Antimony......	Sb	39.7	3	119.1	120.0
47	Iodine	I	125.89	1	125.89	126.85
48	Tellurium......	Te	63.25	2	126.5	127.5
49	Cæsium........	Cs	131.9	1	131.9	132.9
50	Barium	Ba	68.20	2	136.39	137.4
51	Lanthanum	La	45.81	3	137.45	138.5
52	Cerium	Ce	34.75	4	139.0	140.0
53	Praseodymium..	Pr	46.5	3	139.4 (?)	140.5(?)
54	Neodymium ...	Nd	47.5	3	142.5 (?)	143.6(?)
55	Samarium	Sm	49.7	3	149. (?)	150. (?)
56	Gadolinium . ..	Gd	51.87	3	155.6 (?)	156.8(?)
57	Terbium	Tb	52.93	3	158.8 (?)	160. (?)
58	Erbium........	Er	54.9	3	164.7 (?)	166. (?)
59	Thulium.......	Tu	56.5	3	169.4 (?)	170.7(?)
60	Ytterbium	Yt	57.2	3	171.7 (?)	173. (?)
61	Tantalum	Ta	36.3	5	181.6	183.
62	Tungsten	W	91.5	2	183.0	184.4
63	Osmium	Os	47.4	4	189.6	191.0
64	Iridium........	Ir	47.9	4	191.6	193.0
65	Platinum	Pt	48.33	4	193.3	194.8
66	Gold	Au	195.7	1	195.7	197.2
67	Mercury	Hg	99.25	2	198.5	200.0
68	Thallium	Tl	67.51	3	202.6	204.1
69	Lead	Pb	102.67	2	205.34	206.9
70	Bismuth	Bi	68.83	3	206.5	208.1
71	Thorium	Th	57.7	4	230.8	232.6
72	Uranium.......	U	59.45	4	237.8	239.6
73	Helium	He	.....	..	1.98(?)	
74	Argon	A	.....	..	19.8 (?)	
75	Neon	...	.....	..	9.5 (?)	

INDEX

The references are to marginal numbers. Part II is designated by the Roman numeral, and the appendix by the abbreviation Ap. The numbers are the same for the same topics in Parts I and II.

PART II

EXPERIMENTAL ILLUSTRATIONS

RECOMMENDATIONS AS TO NOTES

THE making of notes is a very important item in the study of a subject in the laboratory. The student should early in his course form the habit of writing them carefully, thoughtfully, and systematically. The aim should be to describe the *essential* features of method and of apparatus, then the things observed, then the things learned from the experiment; for every experiment is designed to teach something. The aim should also be to make the description clear, exact, and simple. The following details of plan are recommended: To use a book about six by nine inches in size, one whose leaves will lie flat when opened, with plain, unruled pages; to enter notes only on the right-hand page, leaving the left-hand for topics, corrections, additions, and the numerical work of calculations; to enter *always* the particular topic which the experiment is to illustrate; as a minor item, to enter the date of work; for convenience, to have the name of the owner on the outside of the cover. The notes should be written in final form in the laboratory, and not copied.

It is particularly urged that the student should read *through* the directions for an experiment before starting upon its performance, and that the experiment should precede the consideration of the corresponding topic in Part I.

THE ELEMENTARY PRINCIPLES
OF CHEMISTRY

PART II

EXPERIMENTAL ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Read Part I, Nos. 1–6, before beginning the experiments.

1. Physical Properties of Sulphur

Observe as to odor, color, hardness, form (crystalline 1–6*
—that is, regular geometric form).

To determine its specific gravity: Weigh carefully to 7
tenths about 10 grams of dry sulphur, in small lumps, free
of dust. Weigh a test-tube, filled with water and corked.
Put the sulphur in the test-tube, refill with water, cork,
and weigh (see Appendix, 1).

The specific gravity of sulphur equals the weight of
sulphur divided by the weight of an equal volume of water.
Calculate the specific gravity from the observations made.

Suggest another method for solids; also one suitable for solids 8
which are soluble in water; a method for liquids; for gases.

Electrification.—Rub a large lump briskly on the dry 9
towel, or, better, on some woolen stuff. It becomes electri-
fied and capable of attracting particles, like bits of paper.

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* The marginal numbers are the same for the same topics in both
Part I and Part II.

10   **Effects of heating.**—Heat in a dry test-tube some lumps of *dry* sulphur, the test-tube being about half filled. It is well to make a holder by folding a strip of paper once or twice upon itself, to wrap this about the test-tube and to seize the ends close to the tube with the fingers, or, better, with the tongs (see Appendix, 2). Apply the heat gradually by passing the tube slowly back and forth through the flame. Have a vessel filled with water on the table close at hand. Should the tube crack and the sulphur take fire, hold quickly over the water. Let the temperature rise slowly while the sulphur is *melting.* Note the color. Keep the surface of the liquid in gentle motion; note the *partial*
11-12 *solidification.* Continuing the heat, note the *second lique-faction*, the beginning of *boiling*, and the white dustlike deposit (*sublimate*). Now, as the sulphur is beginning to boil, move the burner to one side; carefully and slowly turn the melted sulphur into the water, moving the tube to and fro so as to string it out. Set aside the tube with the small residue of sulphur and observe it from time to time as it cools (*solidification* and *crystallization*). Examine the portion which has been suddenly cooled in the water (*allotropism*), comparing it with the original. Select a good sample of it, and, without lumping it together, dry it by pressing and rubbing first between folds of the towel, then between absorbent papers (filter papers). Weigh the sample carefully and leave it for twenty-four hours. Does it change in weight in passing from the *plastic amorphous* (see Part I, No. 21/$_6$) to the *brittle crystalline* form?

12/1   *Crystallization from fusion* (see No. 21/$_4$, Part I).—Fuse some dry sulphur in a crucible, keeping the temperature as low as will suffice to melt; let it cool slowly until a crust has formed; puncture the crust and pour out the remaining liquid; break the crucible and note the appearance of the crystals known as *monoclinic* sulphur; examine them twenty-four hours later. (It is recommended that the instructor do this experiment for the class.)

12/2   *Crystallization from solution* (see No. 21/$_4$, Part I).—Dissolve some sulphur in carbon disulphide to saturation, or nearly so, decant (that is,

drain off) or filter the liquid and allow it to evaporate in the hood. Examine the crystals known as *orthorhombic* sulphur; compare with those of the preceding experiment (*dimorphism*). Do they change on standing? As carbon disulphide is very volatile and combustible, great care should be taken to have *no flame near*. (It is recommended that the instructor do this experiment for the class.)

2. Chemical Properties of Sulphur

Burning or combustion.—Ignite a small lump of sulphur **13** (half the size of a pea) on a suitable surface (an earthen saucer serves well). Describe the phenomenon. The gaseous product is *sulphur dioxide ;* observe its odor *cautiously*, and its effect on litmus—conveniently done by sticking a piece of wet, blue litmus paper to the bottom of a beaker and inverting the latter over the burning sulphur. Compare the sulphur dioxide in these respects with the sulphur. If you have a sample of the plastic sulphur, burn and test this in the same manner.

EXPLANATORY NOTE.—An invisible gas, namely, *oxygen*, a constituent of the atmosphere, takes part in this change, combining with the sulphur and forming the sulphur dioxide, which is quite different from both the sulphur and the oxygen.

Behavior with zinc.—Weigh out carefully 3.20 grams of **13/1** finely divided sulphur (sulphur sublimate, commonly called sulphur flowers); also 6.50 grams of finely divided zinc (zinc dust). Mix these thoroughly in a mortar, so that the original powders can not be distinguished (see Appendix, 5). Take out a small portion, about as much as could be heaped on a five-cent piece (putting the remainder well to one side); heat this strongly on the earthen saucer or on the asbestos board by turning the gas flame down upon it, or, still better, on the spatula blade by thrusting it into the flame. *Do this cautiously, as it may flash up somewhat like gunpowder. In experiments like this, the face should never be held over the material.* Describe the phenomenon, note the ashlike product, compare it with the original sub-

stances, sulphur and zinc, by inspection. Does it melt and burn like sulphur?

(*a*) Put a little of the mixed powders from the mortar in a test-tube, half fill with water, then, closing the tube with the thumb, shake it vigorously, and finally let the powder settle (see Appendix, 4). Does the powder dissolve? Do you see the sulphur tend to separate from the mixture with the zinc? In a similar manner shake some of the ashlike product with water. Does it dissolve? Do you see any tendency of the sulphur to separate from the zinc? Does zinc dissolve in water? Does sulphur dissolve in water?

(*b*) Put a small quantity of the ashlike product in a test-tube and add to it a few drops of *hydrochloric acid*, better designated as *hydrogen chloride* (see Appendix, 3). Note the phenomenon of *effervescence* (bubbles of gas in the liquid; how does it differ from boiling?), indicating the formation or liberation of a gas not previously apparent. Note the odor of this gas (*with care, for the substance is very poisonous*) and its effect on a bit of filter paper wet with a solution of lead acetate, and held at the mouth of the test-tube. Does the ashlike product disappear in the acid? If not, warm the tube slightly.

Compare this with the behavior of a little zinc treated in another test-tube with hydrogen chloride in a similar way (does the zinc powder disappear?); also of sulphur thus treated; also of the mixed zinc and sulphur (does this powder disappear?).

EXPLANATORY NOTE.—In this experiment you have brought about a chemical change. Starting with zinc and sulphur, mixing them intimately and applying heat, you have caused the zinc and the sulphur to disappear, and in their place you have a substance which is distinctly different from each of the original substances. This is a change of identity, a chemical change; and with this meaning, the new substance, which for the moment may be designated x, is said to *contain* zinc and sulphur, and the latter are said to be *combined* in the substance x. To the question, Does the substance x contain nothing but zinc and sulphur? the answer will be suggested by the next experiment.

Behavior with iron.—Weigh out carefully 3.20 grams of 13/2 sulphur powder; also 5.60 grams of finely divided iron (iron dust). Mix them thoroughly in the mortar. Take out a portion, ignite it, and compare the product with the iron, with the sulphur, and with the mixture by inspection and by its behavior with hydrogen chloride, as in the preceding experiment. Does the gas which is obtained have the same odor and action on paper wet with lead acetate as in the preceding?

(*a*) Vary this procedure as follows: Put a portion of the mixed iron and sulphur in a dry test-tube, and cork the latter; weigh it and its contents carefully to tenths; then, holding it nearly horizontal, tap it gently so that the powder spreads out in an elongated pile from the bottom of the tube; let the cork lie loosely in the mouth of the test-tube, and heat the other end in the flame just enough to start the action; then remove from the flame. When the action has ceased, let cool, and weigh again with contents. With a little care, you will be able to do this without losing anything from the tube during the operation. Save the product.

Explanatory Note.—Again you have a chemical change. The substance produced (*y*) *contains* iron and sulphur as constituents, but is neither iron nor sulphur; moreover, it contains *nothing but these*, since what you have in the tube after the change weighs no more than the iron and the sulphur which you put in. Iron and sulphur then must be the sole constituents of the substance *y*; zinc and sulphur are likewise the sole constituents of the substance *x*. The first is therefore named *iron sulphide*, and is said to be *composed* of iron and sulphur, and the second is *zinc sulphide*, and is *composed* of zinc and sulphur. The changes by which these are produced fall under a common type, which may receive a general expression, thus: Substance A and substance B became substance A B (*composition*); or, to express it more concisely,

$$A + B = A B.$$
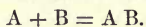
But you have further illustration of chemical change in the production of a peculiar gas by the action of the hydrogen chloride on both zinc sulphide and iron sulphide. This gas is clearly very different from all these other substances. You have noted the same odor and the

same action on the lead paper in both cases, and, in fact, the same gas is produced by both substances. If this is so, evidently neither iron nor zinc can enter into its composition. But the sulphur of one or of the other does so enter, yet the gas is markedly different from sulphur itself and from the gas produced by burning sulphur (see Exp. 13). The sole other constituent of this peculiar gas is hydrogen, which comes from the hydrogen chloride, of which also it is a constituent. The gas is therefore named *hydrogen sulphide*. It is also known as *hydrosulphuric acid.*

13/3   To show that hydrogen sulphide contains sulphur: Place about 1 gram (not more than 2) of the iron sulphide, made in the previous experiment, in the gas generator (see Appendix, 6–9) with just enough water to seal the thistle-tube. Drop the delivery tube into a test-tube about one third filled with *nitric acid* (handle this substance with care, for it is very corrosive *), so that the gas shall bubble through this liquid. Pour a few drops of hydrogen chloride into the thistle-tube of the generator, so as to produce a quick stream of bubbles through the liquid. Place a bit of paper wet with lead acetate over the mouth of the test-tube. As the gas from the generator passes through the nitric acid you see small particles of white or yellowish substance appearing, which, when the action has ceased, or nearly so, will have collected into a mass from which you may rinse the acid with water, and which you may easily recognize as sulphur by inspection and by burning. At the same time the lead paper may, perhaps, show no blackening, since the sulphur is produced only at the expense of the hydrogen sulphide, although enough of the latter to stain the paper may escape destruction by the nitric acid.

EXPLANATORY NOTE.—Hydrogen sulphide, therefore, contains sulphur, and, whenever this gas is produced, it may be taken as evidence of sulphur as a *constituent* in the substances from which it is produced.

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* If nitric acid is spilled on the skin, clothing, or table, the spot should be as quickly as possible moistened with ammonia (side-table), and then rinsed with water.

QUESTIONS.—How can you differentiate (that is, distinguish by differences) between sulphur, and oxygen, and sulphur dioxide? Between zinc, and sulphur, and the mixture of zinc and sulphur, and zinc sulphide? Between iron, and sulphur, and the mixture of iron and sulphur, and iron sulphide? What constitutes the difference, by definition, between a mixture and a chemical compound? (see Nos. 13 and 28, Part I.) How do you bring about the chemical change between sulphur and air, between zinc and sulphur, between iron and sulphur? What evidence by observation have you that heat is produced by these three changes? Does zinc sulphide, made by heating zinc and sulphur, change back to zinc and sulphur by cooling? Does iron sulphide reverse the change by cooling? Is the change from iron and sulphur mixed to iron sulphide accompanied by change in the total weight? (see No. 14, Part I.)

3. Additional Illustrations of Chemical Change

Composition.—Put in a dry test-tube about 1 gram of lead 15/1
dust and 0.2 of a gram of iodine (iodine must be weighed on glass or paper, as it corrodes metal); cork the tube and weigh it with its contents carefully; let the cork lie loosely in the mouth of the test-tube and warm the mixture very slightly, at first barely touching the flame with the bottom of the tube. When the first action is over, the substance may be heated until it melts. A little of the iodine may escape the change, making a purple vapor and a dark deposit on the upper part of the tube. When the tube is cool, weigh it with its content. Describe the phenomenon, and compare the yellow substance with the lead and with the iodine. Preserve a sample of it for future comparison.

EXPLANATORY NOTE.—From lead and iodine is produced a substance which does not give off a purple vapor, nor impart a brown color to water, as does iodine, and which is clearly neither iodine nor lead; yet by the test of weight it can contain *nothing more* than iodine and lead. This bright-yellow substance is named *lead iodide*. Does it dissolve in water?

Composition.—Put about 0.3 of a gram of magnesium 15/2
ribbon, or powder, in the porcelain crucible (see Appendix, 11). Weigh carefully the crucible with its content

and its lid. Support the same on the pipe-stem triangle, and the latter on the iron ring of the stand. Apply the full heat of the flame to the bottom of the crucible for ten or fifteen minutes. Raise the lid slightly to observe what is taking place, but do not let any of the white smoke escape. During the last few minutes the lid should be entirely removed. Let the crucible cool, and weigh it again with content and lid. How do the two weights compare? Describe the phenomenon and compare the substance after heating with the original.*

EXPLANATORY NOTE.—The bright metallic ribbon or powder is changed, simply by heating in contact with the air, to a very different substance—a grayish chalklike powder; but this weighs *more* than the original. It must be, therefore, that something besides magnesium is contained in the product. This "something" comes from the air, is an invisible gas, and is named *oxygen*. The white powder is named *magnesium oxide*. Try also heating a short piece of the ribbon directly in the flame, holding it with the tongs; likewise a little of the oxide.

15/3   **Composition.**—In a similar manner heat in the crucible about 2 grams of zinc dust, weighing the crucible and contents before and after the ignition. Compare the weights and describe the phenomenon. *Zinc oxide* is thus formed—yellow while hot, white when cold. Try also heating a little of the zinc dust on the spatula blade. Preserve a little of the zinc oxide for future comparison.

15/4   **Composition.**—Spread about 4 grams of lead dust on the crucible lid, weighing the whole; then ignite over the flame for fifteen or twenty minutes and weigh again. The reddish-yellow powder is *lead oxide*. Preserve a little of this.

EXPLANATORY NOTE.—The statement made concerning magnesium oxide applies also to zinc and lead oxides.

These four instances of *composition* are changes of the general form: Substance A and substance B become substance A B; or

$$A + B = A B.$$
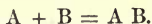
* Clean the crucible by using a few drops of hydrochloric acid, warming gently, then rinsing with water. Scouring with sand may be helpful.

Question.—Have you evidence that, when magnesium changes to magnesium oxide, and zinc to zinc oxide, heat is produced?

Decomposition.—Take a quantity of lead nitrate, about 16/1 1 gram (twice the size of a pea), pulverize finely in a clean, dry mortar, shake the powder into a clean, dry test-tube, wipe off any particles adhering to the upper part of the tube, cork, and weigh the tube and contents. Then, holding the tube nearly horizontal (paper holder), with the cork loosely placed in its mouth, warm the substance gently until the snapping (*decrepitation*) ceases and the powder melts quietly; remove the cork and continue the heating until the bubbling ceases and the glass begins to soften. Note the effect of the brown gas on wet, blue litmus paper. Let cool, and weigh the tube and contents, including the cork. Break the tube and examine the reddish-yellow residue, *lead oxide*. Save a little of this for future reference.

Questions.—Does the residue dissolve in water? Does the lead nitrate dissolve in water? Does the brown gas condense at all on the upper part of the test-tube as you saw in the heating of sulphur? (see Exp. 11.) How does the weight of the residue compare with that of the lead nitrate?

Explanatory Note.—In this experiment you see one substance yielding at least two others, distinctly differing from each other as well as from the original; and at least one of these—that is, the residue in the tube—weighs *less* than the original, which has disappeared, although none of the latter, unchanged, has passed out of the tube. The gas which has passed out, named *nitrogen tetroxide*, and the residue, named *lead oxide* (see Exp. 15/₄), which is left in the tube, must have been *contained* in the lead nitrate which has been destroyed; the latter has been broken up into at least two other substances, each of which weighs less than the original. Such a change is called *decomposition*. It may be described under the general type: Substance A B becomes substance A and substance B; or

$$A B = A + B.$$

Decomposition.—Place about 1 gram of zinc nitrate in a 16/2 test-tube, weigh the tube and contents, then heat. Describe the phenomenon, and note the clear liquid which condenses

on the upper part of the tube. This is water; it is slowly
driven from the tube by heat. Later, note the brown gas,
which appears as in the preceding experiment. This is
nitrogen tetroxide, and it in turn is driven from the tube.
Finally, there is left a powder which no longer melts, and
which is yellow while hot and white when cold. This is
zinc oxide. Weigh again the tube and contents. Examine
the residue left in the tube (comparing with the substance
in Exp. 15/₃), and save a portion for future tests.

QUESTIONS.—Does the residue weigh more or less than the zinc
nitrate from which it comes ? Does it dissolve in water ? Does zinc
nitrate dissolve in water ?

EXPLANATORY NOTE.—You see the substance, zinc nitrate, destroyed
by heat, yielding at least three distinctly different substances—water,
nitrogen tetroxide, and zinc oxide ; and the last of these, and by infer-
ence each of the others also, weighs less than the original substance,
and all of them must have been contained in the original zinc nitrate.
This change falls under the same type as the preceding :

$$A\ B\ C = A + B + C.$$
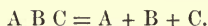
17/1   **Substitution.**—(*a*) Place a small quantity of granulated
zinc, about 0.5 of a gram, in a test-tube ; add to it a few
drops of hydrochloric acid (hydrogen chloride). Note the
effervescence which implies the liberation of a gas. Close
the tube with the thumb for a few seconds, then open it,
holding its mouth to the gas flame. Note what takes place.

EXPLANATORY NOTE.—The colorless invisible gas liberated in this
change burns with an almost invisible flame, and makes with air an
explosive mixture. This causes the slight sound when the content of
the tube is ignited. Larger quantities may be dangerously explosive,
and this fact should always be in mind when dealing with this gas
which is named *hydrogen*.

(*b*) Next, place 1 gram of granulated zinc in a small
evaporating dish which, with a small glass stirring-rod (see
Appendix, 12), has been previously weighed (to tenths is
sufficient). Add about one quarter of a test-tubeful of
hydrochloric acid, in portions at a time, warming some-

what the contents of the dish. Holding a lighted match at the surface of the liquid while the bubbles of hydrogen are breaking, will again show the combustibility of this gas. When the zinc has disappeared except a few black specks, and the bubbles of gas no longer appear, increase the heat somewhat, holding the burner in the hand and touching the tip of the small flame to the bottom of the dish from time to time, as may be needed to keep the liquid quietly boiling (see Appendix, 12). This soon thickens and deposits at the edges. Continue the heating, avoid spattering as much as possible, and soon white fumes appear, and the substance solidifies if cooled. At this point cease the heating and, when the dish is cool, weigh it with its contents. Describe the substance in the dish. Does it weigh more or less than the zinc taken ? Let some of it remain exposed to the atmosphere for a short time and note the change.

EXPLANATORY NOTE.—Hydrochloric acid contains as sole constituents hydrogen and chlorine, the material which you use being this substance dissolved in water. When this is brought in contact with zinc a change takes place, and, when this is complete and the liquid boiled to dryness, the product just seen is the result. Now this weighs more than the zinc, nearly double, and, therefore, must contain something besides zinc; yet it can not contain anything more than zinc, hydrochloric acid, and water; indeed, it can not contain all of these, for hydrogen has passed into the air, as you have seen, and the water also has been boiled away. In fact, the residue in the dish is a substance which contains as sole constituents the zinc used and the chlorine previously contained in the acid, although it is very different from each of these. It is named *zinc chloride*. Exposure of this to the air for a short time will show you incidentally one of its properties; it absorbs water from the atmosphere and liquefies in consequence (*deliquescence*). In this change it is seen that a constituent of hydrochloric acid—namely, hydrogen—leaves the substance, and zinc may be said to take its place ; so that, starting with zinc and hydrogen chloride, you obtain hydrogen and zinc chloride. Such a change is called *substitution*. It may be represented by the general form :

$$A + BC = B + AC.$$
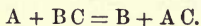
17/2   **Substitution.**—*Optional experiment.*—(*a*) Place about 0.5 of a gram of granulated zinc in a test-tube, add dilute sulphuric acid, warm, and test the gas at the flame as in the preceding experiment.

(*b*) Next place about 3 grams of granulated zinc in the evaporating dish, add about one test-tubeful of dilute sulphuric acid (one volume of concentrated acid to four of water) and an equal volume of water, and warm. When the zinc has disappeared, or nearly so, filter (see Appendix, 13), boil down the liquid somewhat, and set aside to crystallize. Crystals of *zinc sulphate* are thus obtained. The relation of this substance to sulphuric acid is similar to that of zinc chloride to hydrochloric acid.*

17/3   **Substitution.**—Place about 3 grams of lead powder in a small evaporating dish, add about one quarter test-tubeful of nitric acid and an equal volume of water. Heat gently until the action ceases, filter the liquid, and set it aside to crystallize. When there is a considerable deposit of crystals, drain off the liquid, and throw the crystals on two or three thicknesses of filter paper to absorb the adhering liquid. These are crystals of *lead nitrate*. Heat a portion of these and compare the result with that in Nos. 15/$_4$, and 16/$_1$. Save a portion of the crystals, labeled, for later use.

17/4   **Substitution.**—*Optional experiment.*—Dissolve about 10 grams of crystallized copper sulphate in about 50 cubic centimeters (see Appendix, 14) of boiling water, using the larger evaporating dish. Add to this 4 grams of granulated zinc, and boil the liquid gently until the blue color has entirely disappeared. Filter; concentrate the liquid to about one third its volume; filter again if necessary, and set aside to crystallize. What is the reddish-brown powder

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* The irritation which may be caused by the fumes and spray in this experiment, if many are working it at the same time, may be relieved by inhaling moderately the fumes from the bottle of ammonium hydroxide (side-table).

which appears when the zinc is added? Add a few drops of nitric acid to this powder after filtration. What is the substance which crystallizes in the filtrate?

EXPLANATORY NOTE.—Copper sulphate bears the same relation to copper and sulphuric acid that zinc sulphate bears to zinc and sulphuric acid (see Exp. 17/₂)—that is, copper has taken the place of hydrogen as a constituent in sulphuric acid. When zinc is brought in contact with the solution of copper sulphate, the copper, in turn, is displaced, appearing as a powder, which, with nitric acid, reproduces a blue solution; while the zinc, with the sulphuric acid, forms zinc sulphate, crystallizing as seen in Exp. 17/₂. Iron may likewise thus substitute itself for copper as constituent. If the action is allowed to take place slowly in dilute solution, the copper may be deposited as a film on an object of iron, such as a knife-blade. This is called "plating."

Double exchange.—The purpose of this experiment is to **18** illustrate a reaction of the type:

$$A B + C D = A C + B D.$$
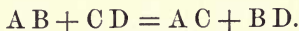
This is known as *double exchange* or *double decomposition;* it is also described as a *metathetic* reaction. The experiment is rather long, so its plan is here given as a whole:

A. To prepare zinc iodide from zinc and iodine :
   (*a*) To show that this is neither zinc nor iodine.
   (*b*) To show that it *contains* both zinc and iodine.
   (*c*) To prepare the solution of zinc iodide in water.
B. To prepare lime sulphide in solution by water from lime and sulphur.
   (*d*) To show that this *contains* sulphur as constituent.
C. To mix the solution of zinc iodide and that of lime sulphide, a chemical change taking place by which a liquid and an insoluble solid are produced.
   (*e*) To show that the liquid now *contains* lime and iodine in combination, but no zinc nor sulphur.

(*f*) To show that the insoluble solid *contains* zinc
and sulphur in combination, but no iodine
nor lime.

Conclusion.—Zinc iodide and lime sulphide have become
zinc sulphide and lime (calcium) iodide.

18/A   A. *To prepare zinc iodide.*—Weigh a clean, small evapo-
rating dish and a short glass rod to tenths of a gram. Place
in the dish 1 gram of granulated zinc and a few drops of
water.

Weigh out 3.9 grams of iodine (on glass or on paper).
Add about one fourth or one fifth of the iodine to the zinc
in the dish, stir, and warm very slightly, just enough to
start the change which itself produces much heat. When
the action seems to cease, add again about the same quan-
tity of iodine, stirring constantly, and so on until all has
been used. This gives a small volume of dark-colored
liquid. Holding the burner in the hand (see Appendix,
12), heat from time to time to keep the liquid gently boil-
ing. There is some escape of purple fumes for a few sec-
onds ; this vapor is irritating, so avoid inhaling it. When
the contents thicken there is a tendency to spatter ; pre-
vent this by constant stirring and moderating the heat.
Finally, when the contents seem thoroughly dry, white
fumes begin to escape. At this point cease heating. The
product is a dry powder slightly brownish in color. When
the dish is cool, weigh it with its contents. The substance
weighs more than the zinc, but somewhat less than the
zinc and iodine together, owing to loss by the heating.*

(*a*) *To show that this is neither zinc nor iodine :* You
have seen that it shows no purple fumes upon heating, as
iodine would show.

Place a small portion, such as would be taken on the
point of a penknife, in a test-tube with a few drops of

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* Iodine stains may generally be removed by using sodium sulphite
or ammonium sulphide.

water. It dissolves as zinc would not, but with no brown color such as iodine would impart.

(*b*) *To show that it contains both zinc and iodine:* Place another small portion in a small evaporating dish, add to it a drop of nitric acid, and heat to complete dryness. You see the purple vapor of iodine, and have left in the dish zinc oxide, as seen in Exps. 15/$_3$ and 16/$_2$.

(*c*) Dissolve the rest of the product, zinc iodide, in 50 cubic centimeters of water (see Appendix, 14). You may see some of the original zinc unacted upon. Filter the solution (see Appendix, 13). Turn a few drops of the filtrate (that is, the liquid which has passed through the filter) into a test-tube, and add a few particles of lead nitrate (see Exp. 17/$_3$) previously dissolved in water. The bright-yellow powder now appearing in the liquid is lead iodide, seen also in Exp. 15/$_1$, and must be taken as further evidence of iodine as a constituent in the substance formed in 18/A. Set aside the remainder of the solution and label it *zinc iodide.* To what type of change does this formation of zinc iodide belong?

B. *To prepare calcium or lime sulphide in solution.*— **18/B** Place 5 grams, roughly weighed, of powdered lime in the larger evaporating dish. Add 100 cubic centimeters of water and boil. Touch a piece of red litmus paper to the liquid and note the effect. Add to the contents of the dish 3.2 grams, roughly weighed, of sulphur powder (flowers) and boil, stirring constantly. Keep the liquid boiling gently for a few minutes, until it becomes colored quite a deep yellow. Cease the heating, and the powder quickly settles to the bottom. Drain off the liquid as much as practicable without disturbing the sediment (this is called *decanting*), pouring the former upon a filter. Add again 100 cubic centimeters of water to the contents of the dish, boil until well colored, let it settle, and decant upon the filter. Do this four times, which will give 300 cubic centimeters or more of clear liquid. This will prob-

ably be enough, but if more is needed, it is only necessary to add another portion of water and repeat the operation. Try the action of this yellow liquid on the red litmus paper.

(d) *To show that sulphur is a constituent of this liquid:* Take about one half test-tubeful, add hydrochloric acid, and heat, holding at the mouth of the tube a piece of filter paper, wet with lead acetate solution. What is the effect? You also see, reappearing in the liquid, yellow, or nearly white, very finely divided sulphur.

The yellow liquid obtained in 18/B may, for present purposes, be considered as a solution in water of *lime sulphide* or *calcium sulphide*, a substance containing lime and sulphur in combination.

18/C   C. *The reaction, double exchange, between zinc iodide and lime sulphide.*—Pour about one half the solution of zinc iodide, prepared in (c), into one of the larger beakers and drop in a piece of red litmus paper. Now, both solutions being hot, pour the lime sulphide slowly into the zinc iodide, a little at a time, constantly stirring, until the paper first turns permanently blue. Be careful to avoid any unnecessary addition of lime sulphide beyond this point. You see a white insoluble solid, a powder, form in the midst of the liquid, and settle to the bottom. A substance formed in this manner is called a *precipitate*, and the operation is *precipitation*.

(e) *To show that the liquid now contains lime and iodine in combination, but no zinc nor sulphur:* Let the precipitate obtained in C settle well to the bottom of the beaker; then, without disturbing it, pour off as much of the liquid as possible upon a filter. Fill up the beaker with warm water, stir the precipitate, let settle, and again decant the liquid upon the filter, collecting what runs through with the first portion. Label this, filtrate (e), and set it aside. Again fill the beaker with water, stir the precipitate, and set this aside to settle, labeling it, precipitate (e).

From filtrate (e) take about one half test-tubeful, and add to this a few drops of lime sulphide solution. The absence of precipitation may be taken as evidence of the absence of zinc, or perhaps, more strictly speaking, of zinc iodide.

Take again one half test-tubeful of filtrate (e), and add a few drops of lead nitrate solution. The bright-yellow precipitate is recognized as lead iodide, and shows the presence of iodine in combination.

Boil the rest of filtrate (e) to dryness in the smaller evaporating dish, having care to moderate the heat as the liquid thickens, so as to avoid spattering and possibly cracking the dish. When the last of the liquid disappears, the full heat of the flame may be applied. As a result, you see the purple vapor of iodine appear. Continue the heating as long as iodine is liberated, and you have left finally in the dish a white, chalklike powder.

That this residue is not zinc oxide, you may see by its color and by adding to the whole, or a portion of it, a very small quantity of water, boiling and testing the liquid with red litmus paper.

That this residue does not contain sulphur, you may see by adding hydrochloric acid, boiling, and testing the vapor by paper wet with lead acetate solution. In fact, it is lime, the substance with which you started.

(f) *To show that the white precipitate* (e) *contains zinc and sulphur, but no iodine nor lime :* Pour the liquid and the precipitate which was labeled precipitate (e) upon the filter. When the liquid has filtered through, fill the funnel with water, not quite up to the edge of the paper, and when this has passed through fill it a second time. The precipitate is thus washed free of soluble matter. Take out a portion of the wet precipitate and dry it by the heat of the flame, holding it on the spatula blade or the asbestos.

Drop some of the dried substance into a test-tube, add hydrochloric acid, boil, and test the vapor as before for hydrogen sulphide.

Drop another portion of the dried substance into a small evaporating dish, barely moisten it with nitric acid, evaporate the acid by gentle heat, then heat with the full flame. You see sulphur appear and burn, but no iodine, and you have left finally zinc oxide, seen also in Exps. 15/$_3$ and 16/$_2$. Boil another portion of the dried substance with a little water, and test by red litmus to see that it is not lime.

EXPLANATORY NOTE.—By the operation in 18/A you have combined zinc and iodine, making zinc iodide; in 18/B you have combined lime and sulphur, forming lime or calcium sulphide; by mixing the solutions of these two substances you have obtained an insoluble solid which contains zinc and sulphur combined—that is, zinc sulphide—and at the same time you have a liquid which contains lime and iodine combined—that is, lime or calcium iodide. Thus the two substances, zinc iodide and lime sulphide, with which you started, have exchanged constituents and produced two entirely different substances. Such a change is expressed by the general form :

$$A B + C D = A C + B D.$$
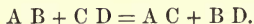
As to Notation.

19   There is used in chemistry, for the purpose of designating substances and describing changes, a system of symbols, which, at this early stage of the study, may best be regarded as a system simply of arbitrary signs, although it really has a much deeper significance. Thus the following symbols are used : For sulphur, S ; for oxygen, O ; for zinc, Zn ; for iron, Fe (Latin, *ferrum*); for hydrogen, H ; for sulphur dioxide, SO_2, signifying qualitatively that it is made of sulphur and oxygen, or contains these as sole constituents; for zinc sulphide, ZnS, and for iron sulphide, FeS, since they contain solely zinc and iron respectively, and sulphur; for hydrochloric acid, HCl, containing hydrogen and chlorine ; for hydrogen sulphide or hydrosulphuric acid, H_2S, since it contains hydrogen and sulphur. The fact that sulphur and oxygen produce by chemical change sulphur dioxide is expressed in equation form thus :

$$S + O_2 = SO_2.$$
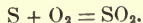
The reactions between sulphur and zinc and iron are thus expressed :

$$Zn + S = ZnS.$$
$$Fe + S = FeS.$$
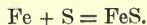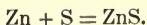
The substance used under the label, hydrochloric acid, is really a **19/1** solution of this substance, HCl, in water. Now, when hydrochloric acid acts on zinc sulphide, the hydrogen of the acid combines with the sulphur of the sulphide forming hydrogen sulphide, and the chlorine of the acid with the zinc of the sulphide forming zinc chloride, $ZnCl_2$; similarly in the case of the iron sulphide. These reactions are expressed by the equations:

$$ZnS + 2HCl = H_2S + ZnCl_2.$$
$$FeS + 2HCl = H_2S + FeCl_2.$$
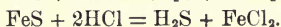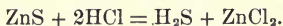
The zinc chloride, $ZnCl_2$, and the iron chloride, $FeCl_2$, remain dissolved in the water. The numerals which you see used in this system of chemical "shorthand" may for the present best be regarded as arbitrary parts of the system. In the "additional illustrations of chemical change" (see Exp. 15/$_1$, etc.) you have used lead, symbol Pb (Latin, *plumbum*), and iodine, symbol I, and lead iodide, symbol PbI_2; magnesium, symbol Mg; zinc, Zn, and oxygen, O; also the oxides of magnesium, zinc, and lead, symbols MgO, ZnO, and PbO.

What is the meaning of the following equations?

$$Pb + I_2 = PbI_2.$$
$$Mg + O = MgO.$$
$$Zn + O = ZnO.$$
$$Pb + O = PbO.$$
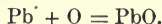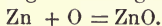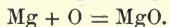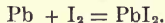
Referring to the experiments under substitution (see Exp. 17/$_1$, **19/2** etc.), you should realize the meaning of this equation, disregarding the numerals:

$$Zn + 2HCl = ZnCl_2 + H_2.$$
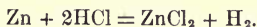
The symbol for sulphuric acid is $H_2[SO_4]$; that is to say, this substance contains hydrogen and something else, the nature of which need not now be considered; this "something" is represented by the symbol in the brackets. The symbol for zinc sulphate is $Zn[SO_4]$, hence the reaction between zinc and sulphuric acid is represented thus:

$$Zn + H_2[SO_4] = Zn[SO_4] + H_2.$$

The symbol for nitric acid is $H[NO_3]$, and of lead nitrate is $Pb[NO_3]_2$; hence the reaction between lead and nitric acid is represented thus:

$$Pb + 2H[NO_3] = Pb[NO_3]_2 + H_2.$$
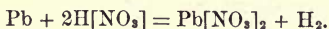
Note that these last three equations fall under the general form

$$A + B C = A C + B.$$

4. Additional Illustrations of Physical Properties

20   **Distillation.**—See Exp. 24/₅, and Appendix, 18, and Part I, No. 12.

20/1   **Sublimation.**—Heat gently a small fragment of iodine in a dry test-tube. Describe the phenomenon. Note the color of the vapor and its odor (cautiously), and its weight compared with that of air (invert the tube). Does the solid melt? Does the vapor pass through the liquid to the solid form on cooling? Is the solid which is deposited (the sublimate) crystalline or not? (See Part I, No. 12.)

21   **Solution and crystallization.**—Add a few drops of hydrochloric acid to a few drops of a solution of lead acetate in a test-tube. What takes place? (Precipitation.) Boil the contents of the test-tube, adding a little water, if necessary, to dissolve the white powder first formed; set aside to cool. What takes place on cooling?

> EXPLANATORY NOTE.—The white powder formed on mixing the two liquids is lead chloride (symbol, $PbCl_2$). Does its formation involve a physical change or a chemical change? It is not soluble, or only slightly so, in cold water; hence it appears as a solid, a powder, in the midst of the liquid. Lead chloride dissolves in hot water, and, as the solution cools, reappears in crystalline form; this is a purely physical change.

21/4   **Solution and crystallization.**—Dissolve about 10 grams of alum (a porcelain evaporating dish is convenient) in 50 cubic centimeters of hot water. Filter the solution. Dissolve about twice as much copper sulphate in a similar manner. Filter this. Mix the two solutions; boil down to about one half the volume, and set aside to crystallize (it may be left until the next day). Can you distinguish the two substances in the crystals? Can you distinguish them in the solution?

21/7   **Water of crystallization.**—Put about 1 gram of copper sulphate crystals in a dry test-tube, and weigh carefully the tube and contents; to tenths is sufficient. Heat slowly, holding the tube so that the open end is a little the lower.

What condenses on the cooler portion of the tube? When the liquid has disappeared let the tube cool, and weigh again. Shake out the white *dehydrated* substance, and let a drop of water from the finger come in contact with a portion of it. Observe carefully what takes place. Bring a drop or two of alcohol in contact with another portion. The dehydrated, *amorphous* substance may be redissolved with hot water, and crystallized as it was at first. (See Part I, No. 21/$_6$.)

Heat in similar manner some alum crystals, also some crystals of potassium dichromate, or of potassium nitrate.

Efflorescence and deliquescence.—Expose to the air for 21/8 twenty-four hours, more or less, (*a*) some crystals of sodium carbonate or of sodium phosphate; (*b*) some calcium chloride or sodium hydroxide (see also Exp. 17/$_1$ b).

Heat of solution.—Determine the effect on temperature 22 (see Appendix, 15) of dissolving in water (*a*) some common salt—that is, sodium chloride (use a beaker half filled with water and about a tablespoonful of salt); (*b*) some sodium hydroxide; (*c*) some hydrochloric acid (concentrated).

Melting point, determination of (see Appendix, 16).—De- 23 termine the melting point and freezing point of paraffin thus: Prepare a tube of thin wall and small bore by heating in the flame a piece of glass tubing, an inch or two from its open end, until the glass is well softened; then, drawing it out slowly until the bore becomes quite small, and finally applying the flame at the narrow part and separating completely the two portions of the tube. The narrow end is thus closed by fusion. Put into this a few bits of paraffin; warm just enough to melt the latter; shake or jar the tube so that the liquid shall completely fill the narrow portion, leaving no air bubble. With a rubber band attach the tube alongside the thermometer so that the paraffin is about opposite the bulb. Suspend the thermometer and tube over a beaker of water which is supported on an asbes-

tos board or a wire gauze, so that the bulb and paraffin shall be well immersed. Slowly heat the water and observe the temperature when liquefaction is first noted. When this is complete, let cool, and observe the temperature when solidification begins. Repeat four or five times, until the several readings of each point are fairly concordant. As the melting or the freezing point is approached the temperature should be allowed to change *very slowly*, and the water should be well stirred. The freezing point may be somewhat lower than the melting point, due to *surfusion*.

24   Boiling point, determination of, and conditions affecting.— Determine the boiling point of water thus (see Appendix, 17) : Use a distilling flask of about 200 or 225 cubic centimeters capacity, with a side delivery tube carrying a short piece of rubber hose. Half fill with water. Through the stopper insert a thermometer (wetting it first) so that the bulb is below the exit and above the surface of the water, high enough to avoid being spattered during boiling. Support the whole on asbestos, or gauze, and the iron stand so that there may be no danger of overturning. Heat until the liquid boils and the temperature reaches its maximum, which is steadily maintained for five minutes or more. This is the *boiling point*. It should be, with a good thermometer, 100° C.; but thermometers are often inaccurate, and may be corrected by actual observation, made with due care.

Vary the experiment as follows :

24/1   1. By pinching with the tongs, close the rubber exit tube while the liquid is still boiling, and note the effect on temperature. Let it rise only about 2°, then open and observe what takes place.

24/2   2. Lower the thermometer until the bulb is immersed, boil, and note again the maximum temperature, first with the tube open, then with it closed. The temperature of the boiling liquid is likely to be higher than that of the vapor under similar conditions.

3. Let it cool sufficiently, then add to the water about 24/3 a tablespoonful of salt and a few crystals of copper sulphate, boil, and observe the temperature of the vapor as before (it should be unchanged).

4. Lower the thermometer and take the temperature of 24/4 the boiling solution.

Collect some of the liquid (*distillate*) which drops from 24/5 the exit tube. Does it show any color? Has it the taste of salt? (*Distillation.*)

Fit a test-tube well with a cork, fill about one third with 24/1 a water, and boil. After it has boiled a few seconds and while it is still boiling, remove from the flame, quickly insert the cork, invert the tube, immerse the stoppered end just under the surface of some water in a convenient vessel, and pour cool water on the upper end. What takes place? What is the explanation of the phenomenon? Let cool, uncork, and note the inrush of air. If the cork does not come out easily, force a pin between the cork and the glass and withdraw it.

Optional experiment.—In a small evaporating dish evapo- 25 rate to dryness some distilled water. Is there any residue?

Similarly evaporate to dryness some sample of natural water. Is there a residue?

CHAPTER II

EXPERIMENTS ILLUSTRATING THE FUNDAMENTAL QUANTITATIVE LAWS OF CHEMICAL CHANGE

33 Note.—Study with special care the quantitative relations in the experiments of this chapter. In all the measurements of quantity which you make, whether in this work or in the work of subsequent chapters, try to make an estimate of the uncertainty which is necessarily involved in the measurements by reason of the conditions in which you work. In some of the problems it will be important to make at least two measurements of the same quantity, in order to show how much uncertainty is thus involved. As the work advances, after you have studied the primary topic which is illustrated, give some thought to the topics already passed, which may find secondary illustration by the experiment in hand, especially as to these general laws, and also as to the kind of reaction involved, and other definitions presented in Chapter I.

Have care always to state in your notes the specific topic to be illustrated, and, when practicable, the specific experimental problem to be solved; then describe your method of solution, endeavoring to give the essential features, apparatus, incidental observations, etc.; then, as a rule, present the data of observation, carefully labeled, the calculations, if any, and the final result, with your conclusions therefrom.

In recording data, be sure that your notes include all original observations. For example, you are to determine the weight of a substance contained in a dish; you do so by determining the weight of the dish with its contents, and the weight of the dish alone, the difference between these being the weight sought. Now, the important point is to record in your notes, not simply this difference, but the original weights which by subtraction give the desired value.

Notes should be written in the laboratory, during the progress of the experiment, and quantitative data should be recorded *at once.* Do not rush through an experiment and then try to write up your notes from memory, perhaps outside the laboratory. Do not delay recording results until you have learned whether they are good. Put them all

24

down, and later mark " erroneous," if necessary.   Do not be discouraged if the result at first trial is unsatisfactory. You will often need to perform an experiment once to learn how to do it, and need to repeat for successful results. It is well to bear in mind that practical chemistry is more or less a handicraft, and that you will surely fail to get good return for your time and labor unless experiments are performed carefully as well as studiously.

Make it a rule to read through the directions for the *whole* experiment before you start upon its performance.

1. The Law of Persistence of Mass

A. **Preliminary.**—Some apparent contradictions :

(*a*) Place about 1 gram of mercury sulphocyanate in 34/1 a small evaporating dish, counterpoise the dish and its contents on the balance, ignite the substance by a match or a hot iron wire.   Describe the phenomenon, and note the effect on the equilibrium of the balance. Had you made the experiment without using the balance, what would you have inferred as to the effect of the change on the quantity of substance ?

(*b*) *An experiment for the teacher to perform before the* 34/2 *class.*—Burn a taper, or alcohol in a small lamp, in such manner as to collect and weigh the products of combustion. This may be conveniently done as follows : Suspend the taper or very small lamp (which can be made from a short test-tube, a cork, and a piece of wicking) from the lower end of a student-lamp chimney, to the upper end of which is fitted a perforated cork carrying a train of four absorption tubes ; the first two of these are filled with fragments of sodium hydroxide, and the last two with fragments of calcium chloride ; to the farther end of the train is attached a rubber hose leading to a filter pump or to an aspirator ; the whole apparatus—lamp, chimney, and absorbing train—is then suspended from the arm of a suitable balance and counterpoised. When this is ready, start the pump which draws a current of air through the apparatus,

carrying with it the products of combustion into the tubes, where they are retained. Light the lamp and allow it to burn fifteen or twenty minutes, noting the effect on the
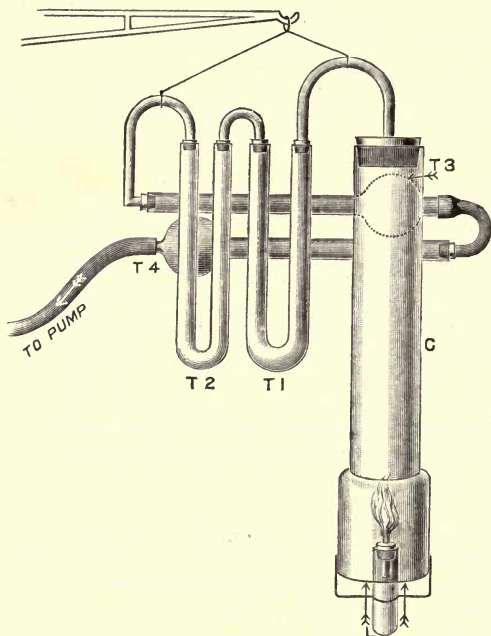

FIG. 1.—Diagram of apparatus for Exp. 34/2. *L*, alcohol lamp; *C*, lamp chimney; T_1, T_2, T_3, and T_4, absorption tubes.

equilibrium of the balance. How does the weight of the products of combustion compare with the weight of the material burned? (Fig. 1.)

34/3   *An alternative form* of apparatus for this experiment may be more simply provided as follows: Make a cylinder of wire gauze which shall fit closely in the upper half of the student-lamp chimney; fit the lower end with a cork, through which several holes are bored, and to which a short piece of taper may be attached (see Fig. 2), or, preferably,

suspend the little alcohol lamp as in Fig. 1.   Fill the gauze cylinder with fragments of sodium hydroxide, and suspend the whole by a loop of wire from the arm of the balance.

Light the lamp or the taper.   Although the products of combustion are not so fully retained as in the preceding form, the gain in weight is made evident by burning for a few minutes.

34/4

EXPLANATORY NOTE.—The alcohol and the candle contain carbon and hydrogen as elementary constituents.   These in the process of burning combine chemically with the oxygen of the air, forming as products gaseous carbon dioxide and hydrogen oxide—i. e., water.   These products are carried into the tubes, where the carbon dioxide is retained by the sodium hydroxide, and the water is retained partly by condensing to liquid form, and partly by the strongly hygroscopic substance, calcium chloride.   The products of the combustion, therefore, weigh more than the material burned by just the weight of the oxygen taken into combination from the air.

FIG. 2.

All the ordinary fuels likewise contain carbon and hydrogen; therefore the products of ordinary combustion are carbon dioxide and water, and combustion itself is simply an instance of chemical action accompanied by heat and light.   (Compare with Exps. 13, 15/$_2$ and 15/$_3$.)

B. **To illustrate the law:**

(1) Recall or repeat Exps. 13/$_{2a}$, and 15/$_1$.

(2) In a gas generator (see Appendix, 6) fitted with a 34/5 thistle-tube and a delivery tube place a charge of marble (i. e., calcium carbonate, symbol $CaCO_3$) in small lumps, with enough water to seal the end of the thistle-tube; in another vessel (a bottle or a deep beaker) place a strong solution of sodium hydroxide; in a third (a small beaker), some concentrated hydrochloric acid and a glass rod. Counterpoise the three vessels with their contents on the heavier balance (see Appendix, 1, A).   Cautiously turn the acid, a few drops at a time, into the generator (observe
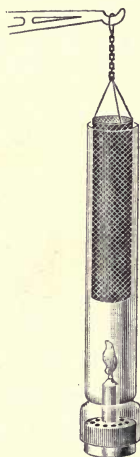
what takes place), letting the reaction go on slowly through a measured interval of time while the delivery tube opens into the air, and until the effect on the equilibrium is unmistakable. (What is the effect?) Then drop the delivery tube into the second vessel so that the gas bubbles through the solution; again counterpoise, and continue the reaction at about the same rate, and during the same length of time as before; then again note the effect on the equilibrium.

35   **Secondary observation.**—To show that an invisible gas, quite different from air and not before present, is produced by this change, remove the material from the balance, drop the delivery tube into a clean beaker or bottle, partly covered by a glass plate (see Appendix, 19, V), and pour a little more acid into the generator. After the effervescence has continued a few seconds, slide the plate to one side and plunge a lighted match into the bottle. The gas produced is *carbon dioxide*, symbol CO_2.

36   EXPLANATORY NOTE.—This experiment, owing to the limitations in weighing, can give but crude quantitative results, showing simply that the balance, which gives no indication of differences less than 0.2 or 0.3 of a gram, indicates unmistakable loss of weight in the first conditions, but no loss in the second, although the reaction goes on as in the first.

The chemical name of marble is calcium carbonate, symbol $CaCO_3$. It is a salt derived from the metal, calcium, and carbonic acid, symbol H_2CO_3. By the action of hydrochloric acid on this substance, calcium chloride, another salt, symbol $CaCl_2$, is produced, and carbonic acid. The latter substance breaks up at once into carbon dioxide, symbol CO_2, and water. symbol H_2O. The carbon dioxide passes into the atmosphere as an invisible gas, the water adds itself to the rest of the water, and the calcium chloride remains in solution. These two reactions are expressed in equation form as follows:

$$\text{(1)} \quad CaCO_3 + 2HCl = CaCl_2 + H_2CO_3.$$
$$\text{(2)} \quad H_2CO_3 = CO_2 + H_2O.$$
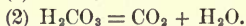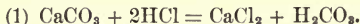
Sodium hydroxide, symbol $NaOH$, is a base (see Part I, 30/₂), and when the carbon dioxide comes in contact with its solution in the sec-

ond bottle the two substances combine and another salt is produced, namely, sodium carbonate, symbol Na_2CO_3. This remains in solution. The following equation expresses this reaction:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

2. The Law of Fixed or Definite Proportions

(*a*) Evaporate to dryness a few drops of hydrochloric **37** acid solution in the small evaporating dish, heating gently with the caution necessary in this operation (see Appendix 12). Acid of a good degree of purity is needed.

(*b*) Likewise evaporate a few drops of ammonium hydroxide solution. Describe the results.

(1) Carefully weigh to tenths of a gram the small porcelain dish with a short glass rod, both articles being clean and dry.

[It will be advantageous to have two or even three weighed dishes to use. They may be distinguished by scratches on their edges made with a file.]

With some suitable measure (a test-tube with a slip of gummed paper or a file scratch on its side will serve, although a burette or graduated pipette is better) take two equal volumes of the ammonium hydroxide solution, pouring them into a weighed dish. Exactly neutralize this liquid with the hydrochloric acid solution, using litmus paper as indicator, and adding the acid drop by drop, stirring after each addition, until the paper just turns permanently pink. Note carefully the volume of acid used. Evaporate the contents of the dish to dryness on the waterbath; this is facilitated by frequent stirring toward the end of the operation. Let cool, and determine the weight of the salt obtained. How will you make sure that the salt is completely dried?

Redissolve the salt, using very little water; filter if necessary, and crystallize. Dry the crystals on filter paper, and test them with blue and with red litmus paper slightly wet.

(2) Take the same volume of hydrochloric acid which was used in (1), add to it only one measureful of ammonium hydroxide, evaporate, and weigh as before the salt obtained. Redissolve, filter, and crystallize this salt. Test the crystals with red and with blue litmus paper.

(3) Take again the same volume of acid as previously used, add to it three measurefuls of ammonium hydroxide, evaporate, and weigh as before.

Redissolve, filter, and crystallize this salt. Test the crystals with red and with blue litmus paper.

38   QUESTIONS.—Are the three portions of salt thus obtained different samples of the same substance, or are they different substances? What is the ratio between the quantities of salt obtained in the three cases? Have you any evidence that hydrochloric acid or ammonium hydroxide passes off during the evaporation, in (1)? in (2)? in (3)? What is the logic of the experiment? Reason it out fully. Is heat liberated when hydrochloric acid and ammonium hydroxide are mixed?

39   EXPLANATORY NOTE.—The salt obtained by the combination of hydrochloric acid and ammonium hydroxide (symbol NH_4OH, a base) is named ammonium chloride, symbol NH_4Cl, and the reaction is thus expressed: Hydrochloric acid and ammonium hydroxide produce ammonium chloride and water; or in equation form,

$$HCl + NH_4OH = NH_4Cl + H_2O.$$
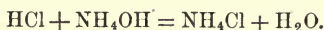
3. The Law of Multiple Proportions

40/a   (a) Take of iodine and of mercury in the ratio of 252 parts by weight of the former and 199 of the latter; for the actual experiment weigh out accurately (in some glass vessel, as both substances attack metals) 6.30 grams of iodine, and 5.00 grams of mercury. Transfer the mercury to a mortar (previously weighed with its pestle on the heavier balance). Add a few drops of alcohol, then a small portion of the iodine, and rub gently with the pestle; then add another portion of iodine, and rub; and so on until all the iodine is used and the whole is thoroughly mixed.

It is well to keep the mixture slightly moist with alcohol during only the first stages of the operation, in order to avoid overheating, otherwise there may occur a slight flash in the mortar, accompanied by the fusion of the substance. If this happens, it is better to clean the mortar (use sand to scour), and start the experiment anew. Avoid inhaling the fumes of iodine, and protect the hand, if desired, with a fold of the towel. Iodine stains may be removed with sodium sulphite or ammonium sulphide.

Persistent rubbing may be necessary even after the substances seem well mixed. The operation when completed should yield a bright-red powder, mercuric iodide, symbol HgI_2.

Weigh the mortar and contents on the heavier balance.

Take out a small sample and apply alcohol to it in a **40/1** test-tube. [The alcohol should not be colored by the iodine; if it is so colored, continue the rubbing.] Warm the alcohol to gentle boiling, having care that the alcohol vapor is not ignited by the flame; set aside to cool. The amorphous powder dissolves in hot alcohol, and deposits on cooling in crystalline scales, sometimes bright scarlet, sometimes yellow (allotropic forms).

Sublime another small portion of the red powder in a **40/2** dry test-tube, note the red and yellow sublimate (allotropic forms); rub the yellow with a glass rod. Note the crystalline residue after fusion.

(*b*) Take 5.60 grams of mercuric iodide obtained in **40/b** (*a*), which is equal to ½ (6.3 + 5) and 2.50 grams of mercury. Add the mercury in small portions at a time to the mercuric iodide in a mortar, rubbing thoroughly after each addition. This should yield a greenish-yellow powder (mercurous iodide, symbol HgI). If the color is not satisfactory, continue the rubbing and, perhaps, allow to stand for twenty-four hours.

Weigh the mortar and contents on the heavier balance.

Treat a small portion as in (*a*) with boiling alcohol. **40/3** Does it dissolve?

40/4   Sublime another portion; note the character of the sublimate and the residue after heating.

40/5   EXPLANATORY NOTE.—Mercurous iodide is insoluble in hot alcohol and decomposes on heating into mercuric iodide and mercury.

QUESTIONS.—How do you differentiate between mercury and iodine mixed, and mercuric iodide? between mercuric iodide and mercurous iodide? between mercuric iodide and mercury mixed, and mercurous iodide? How does the weight of the mercuric iodide obtained compare with that of the mercury and iodine used? What becomes of the alcohol? How does the weight of the mercurous iodide compare with that of the mercuric iodide and the mercury used? What is the ratio between the quantities of mercury in the two substances reckoned for constant quantity of iodine? between the quantities of iodine, reckoned for constant quantity of mercury? What is the logic of the experiment? Show clearly that it is not contradictory to Law 2. What does Law 2 affirm in regard to these two reactions? What does Law 1 affirm with regard to them? Is heat liberated in the reaction between mercury and iodine?

4. The Law of Equivalent Proportions *

41   **General problem.**—To investigate the relation between those quantities of different substances which produce equal chemical effects.

Specific illustrative problem.—A. To determine the relation between the quantities of oxygen which combine respectively (1) with 2.40 grams of magnesium, and (2) with 6.50 grams of zinc.

B. To determine the relation between the quantities of hydrogen liberated from hydrochloric acid respectively (3) by 2.40 grams of magnesium, and (4) by 6.50 grams of zinc.

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* Inasmuch as the experiment under this topic involves the measurement of gas-volume, the instructor may prefer to introduce the laws of Boyle and of Charles, Chapter IV, at this point. The writer prefers to give them simply as arbitrary rules and to study them later, rather than to interrupt the logical development of this chapter.

A 1

To determine the quantity of oxygen which combines 41/1
with 2.40 grams of magnesium : Recall Exp. 15/2. Weigh
to hundredths of a gram a porcelain crucible with its lid,
clean and dry. Weigh out exactly 1.00 gram of magnesium
ribbon. Breaking this into small pieces, transfer the whole
to the crucible. Support the latter, covered by its lid, on
the pipe-stem triangle and iron stand (see Appendix, 11).
Apply heat, slowly at first, then the full heat of the flame.
Raise the lid slightly from time to time to see what is
taking place and to let air in, but avoid losing any of the
white smoke. When the danger of this is passed, remove
the lid and continue the heating about fifteen minutes.
When the crucible is cool, weigh it with its lid and con-
tents to hundredths. To make sure that the reaction is
complete, heat, cool, and weigh again. When heated, the
magnesium combines with the oxygen of the air and the
product is magnesium oxide, MgO. Calculate from the
mass of oxygen which combines with 1.00 gram of mag-
nesium what mass combines with 2.40 grams of the same.
(Upon what law is this calculation based?) At least two
determinations of this value should be made.

Secondary items.—Describe the phenomenon seen and 41/a
the substance produced. Does the reaction evolve heat?
Does magnesium oxide dissolve in hot water? Test with
red litmus paper. Does it dissolve in dilute sulphuric acid?
Boil it in the crucible or dish with a very little of the dilute
acid, filter, and crystallize the salt, magnesium sulphate,
$MgSO_4$ (compare Exp. 17/2). How does the reaction be-
tween magnesium oxide and sulphuric acid, symbol H_2SO_4,
differ from that between magnesium and the same acid?

An Alternative Method

This method involves making, first, magnesium iodide, MgI_2, then 41/b
heating this substance, by which it is decomposed into iodine and mag-

nesium, and the latter is converted into the oxide, MgO, all without loss of substance other than the iodine. The final result is the same as in 41/1, but it is brought about with less elevation of temperature.

Weigh to hundredths a small evaporating dish with a short glass rod. Weigh out carefully 0.50 of a gram of magnesium, and place this in the dish. Weigh out about 5 grams of iodine. Pour on the magnesium enough alcohol to cover it. Then add the iodine, a little at a time, stirring constantly. With a little care the reaction may be so controlled that the heat evolved shall not cause spattering and consequent loss of material. When the magnesium is entirely acted upon, heat the dish and contents on the water-bath until only a thick, siruplike mixture is left. Then transfer the dish to the iron ring and heat with a very small flame, holding the burner in the hand (as before directed for careful evaporation ; see Appendix, 12), and stirring constantly. Continue this until the danger of spattering is past, then apply the full heat of the flame. As this causes iodine fumes, it may be necessary to perform this part of the experiment in the hood. Continue the heating for a few minutes after the iodine has entirely disappeared. Finally let cool, and weigh the dish and content, which is magnesium oxide, a fine powder only slightly brown in tint. The calculations are the same as in the first method.

A 2

41/2   To determine the quantity of oxygen which combines with 6.50 grams of zinc :

It is impracticable to do this by direct combustion, as in the magnesium experiment. The method is to act on zinc with nitric acid, produce zinc nitrate, dry this, then ignite it and thus produce zinc oxide without loss of other than volatile material. Refer to Exps. 15/3 and 16/2.

Weigh a small evaporating dish with a short glass rod to hundredths of a gram. Weigh out 2.00 grams of granulated zinc. Transfer the latter to the dish. Pour a drop

or two of nitric acid down the rod, letting it come slowly in contact with the zinc. (Remember that nitric acid is very corrosive.) When the first violent reaction is over, add a few drops more of acid, and so on until the zinc is completely dissolved with the least acid that will serve. Evaporate the contents of the dish to dryness on the water-bath. The evaporation may be performed more quickly, but only with closer attention, by holding the burner in the hand, having the flame low, and applying just enough heat to keep the liquid gently boiling, until there is danger of spattering, and then not enough heat to cause the formation of bubbles (see Appendix, 12). When the salt is thoroughly dry, increase the heat, and finally give it the full flame for about fifteen minutes. When the reaction is finished, let the dish cool, and weigh it with its contents to hundredths of a gram. The product is zinc oxide. To make sure that the reaction is complete, heat, cool, and weigh again. From the mass of oxygen which combines with 2.00 grams of zinc, calculate what mass combines with 6.50 grams of the same. At least two determinations of this value should be made.

Secondary items.—Describe the reaction between zinc and 41/c nitric acid. Is heat evolved? What takes place when zinc nitrate is heated? Does zinc oxide dissolve in water? in dilute sulphuric acid? Optional experiment: Filter, and crystallize the zinc sulphate (see Exp. 17/2).

How does the reaction between zinc oxide and sulphuric acid differ from that between zinc and the same acid? What is obtained by the action of hydrochloric acid on zinc oxide?

Summary.—Compare with each other the individual 41/d quantitative results with magnesium, also those with zinc; then compare the average of the first with the average of the second. What is the conclusion as to the masses of oxygen which combine respectively with 2.40 grams of magnesium and with 6.50 grams of zinc?

B 3

41/3   To measure by volume and calculate into weight the quantity of hydrogen liberated from hydrochloric acid by 2.40 grams of magnesium :

(*a*) To measure the capacity of the collecting bottle, No. x (a bottle with glass stopper holding about 2,500 c.c.): Fill the tank with water, which should be brought to the temperature of the room, if necessary by heating portions in the iron vessel. Fill the collecting bottle completely and put the stopper in place. Measure the volume of this water in cubic centimeters ; this may be done by pouring, without loss, into a graduated cylinder, or, if such vessel is lacking, as follows : Fill a graduated flask repeatedly from the bottle (one holding 750 c.c. is convenient), and weigh, in a vessel not unnecessarily large or heavy, the last residue which is insufficient again to fill the flask ; the weight of the water in grams may be taken with only inconsiderable error as its volume in cubic centimeters. Determine thus the capacity at least twice. The variations should not be more than one or two cubic centimeters.

[Why not weigh at once the bottle filled with water?]

41/3b   (*b*) To generate the gas : Weigh out carefully 2.40 grams of magnesium ribbon, transfer without loss to the gas generator (see Appendix, 6). Add water just sufficient to seal the thistle-tube ; test for leakage by blowing in the exit end of the delivery tube until the water rises four or five inches in the thistle-tube, then pinching the rubber hose, or closing the end of the tube with the tongue. The column of water should maintain its height, or sink only slowly. A film of water between stopper and glass will help to prevent leakage, or, as a last resort, the stopper may be sealed with vaseline or with paraffin.

Have some strong hydrochloric acid in a beaker. It will be found convenient to let a test-tube lie in the bulb of the thistle-tube ; it may be used like a rod to aid in

pouring from the beaker, and the rounded end makes a kind of valve.

(c) To collect and measure the gas : Fill the collecting **41/3c** bottle with water, put in the stopper, invert in the tank, remove the stopper, incline the bottle so that it rests on the wall of the tank and slip into its mouth the bent delivery tube (compare Appendix, 19, I).   Pour acid, a little at a time, into the thistle-tube until no more gas is generated. As much heat is liberated in this reaction, it is well to set the generator down into the water of the tank.   Ascertain now or later the volume in cubic centimeters of the acid turned in.

When the effervescence ceases, raise the bottle so that the water within and without is as nearly as practicable at the same level, withdraw the delivery tube, insert the stopper under water, and remove the bottle from the tank. Measure the volume of the water left in the bottle, and calculate the volume of the gas collected.

Observe the temperature of the water in the tank, which should be that of the room, so that it may be safely assumed that the temperature of the gas is the same.

Observe by the barometer the pressure of the atmosphere (see Appendix, No. 15 B).

Take note *that hydrogen with air may make a dangerously explosive mixture ; therefore have great care that the hydrogen is not brought near a flame.*

Calculations.   (See Appendix, 20.)—The data of this **41/3d** problem are :

The weight of metal used ;

The total capacity of the bottle ;

The volume of acid turned in (how is this used ?) ;

The volume of water left in the bottle ;

The temperature and pressure of the gas.

From these is first calculated the volume of the gas generated, measured in cubic centimeters at the observed temperature and pressure.

20

Now, since change of temperature and change of pressure cause change in the volume of gases, it is important that observed volumes, in order to be comparable, should be reduced to standard conditions of temperature and pressure. It is customary to use as standards 0° C. for temperature and 760 millimeters of mercury column in the barometer for pressure. The method of reducing observations to the standards may be taken arbitrarily now, to be explained in Chapter IV. The observed volume is reduced to volume at 0° by applying the law that "a volume of gas at 0° increases by $\frac{1}{273}$ of itself for each degree of rise in temperature, pressure remaining unchanged." The observed volume is reduced to volume at 760 mm. by multiplying by the observed pressure in millimeters and dividing by 760; but since the gas is collected and measured over water, it is saturated with water vapor, and the observed pressure is made up of the true pressure of the gas plus the pressure of the vapor at the given temperature. The pressure or tension of the water vapor at different temperatures is obtained by observation, and given in tables accessible in books of reference; this value for the ordinary temperature of 20° is 17 mm., and may be subtracted from the observed pressure as a slight correction. (See Appendix 22.)

The volume of gas generated, thus brought to standard conditions, is finally calculated into weight, by aid of the fact that one liter of hydrogen at 0° and 760 mm. weighs 0.0899 of a gram. Does the fact that the hydrogen collected in the bottle is mixed with air coming from the generator affect the problem?

At least two fairly concordant determinations should be made of the hydrogen by magnesium.

B 4

41/4   To measure by volume and calculate into weight the quantity of hydrogen liberated by 6.50 grams of zinc (compare Exp. 17/₁): Proceed as in B 3, (*b*) and (*c*), using 6.50

grams of granulated zinc. At least two fairly concordant determinations of this value should be made.

Summary.—Compare with each other the individual 41/5 results from magnesium; also those from zinc; then the average of the first with the average of the second. What is the conclusion as to the quantities of hydrogen liberated respectively by 2.40 grams of magnesium and by 6.50 grams of zinc? Compare the results in A and B. Are the masses of magnesium and zinc which produce equal chemical effect in combining with oxygen also the masses which produce equal effect in liberating hydrogen?

5. The Law of Gas-volumetric Proportions

General problem.—To determine the proportions by volume in which gaseous substances react.

Specific illustrative problem.—To investigate the propor- 47 tion by volume in which nitrogen dioxide reacts (1) with air and (2) with oxygen.

EXPLANATORY NOTE.—The plan of work under this topic must be to state first the fundamental fact involved, and to let the experiment serve rather to illustrate the practical application of this fact to the observations in hand.

Nitrogen dioxide, symbol NO (named also nitric oxide), combines with oxygen on contact in the ratio of 4 volumes (gaseous) of the former to 2 volumes (gaseous) of the latter, forming 2 volumes (gaseous) of *nitrogen tetroxide*, symbol N_2O_4, a substance which is soluble in water. Air is a mixture of oxygen and nitrogen, 1 volume of the former to 4 volumes of the latter. Nitrogen does not react with nitrogen dioxide.

(*a*) To calibrate two gasometric (i. e., gas-measuring) 47/a tubes: Use two test-tubes, 230 mm. (9 in.) long and 18 mm. ($\frac{3}{4}$ in.) wide, and as a unit tube one about 44 mm. ($1\frac{3}{4}$ in.) long and 10 mm. ($\frac{3}{8}$ in.) wide. Divide the large tubes into portions of equal capacity by filling the small tube with water, pouring its content into the large tube, and marking the level of the water with a rubber band.

47/b   (*b*) To prepare nitrogen dioxide : Put into the generator a charge (to about half fill) of *ferrous sulphate* (commercially known also as copperas and as green vitriol) in small lumps, with water just enough to seal the thistle-tube. Have strong nitric acid with a rod in a small beaker. Turn the acid a little at a time into the generator. Collect the gas over water in the small collecting bottles (see Appendix, 19, I), rejecting, as probably impure, the first three or four bottlefuls ; then retain for use stored in the bottles. *Carefully avoid inhaling the gas; also handle the acid with care, as it is very corrosive.*

47/1   (1) By means of the gasometric tubes, measure out volumes of air and of nitrogen dioxide in the ratio of 5 : 2 ; pouring the latter under the water of the tank, upward from the bottle into the tube (see Appendix, 19, II). It is advantageous to use large rather than small quantities.

Pass the content of one tube, under water, into the other (what takes place ?), and, after sufficient interval, read the volume of the residual gas. Repeat the operation enough to get fairly concordant results. If the gas is pure and the measurements well made, the result is 4 volumes in proportion to the 5 and the 2 which were taken ; therefore 3 volumes, or ¾ of the mixture, disappear in the reaction. (What is the cause of this contraction ?)

Take a measured sample of the residual gas, add to this a measured volume of air, and observe the contraction ; if it is not zero, make repeated additions, until there is no further contraction.

Take another measured sample of the residual gas, add to it a measured volume of nitrogen dioxide ; if the contraction is not zero, continue the additions until it is.

Does the first residual gas contain oxygen ? Does it contain nitrogen dioxide ? What is it ?

47/2   (2) Measure out, as in (1), volumes of oxygen and of nitrogen dioxide in the ratio of 1 : 2. Mix them and measure the residual volume and the contraction.

If there is a residual gas, test it for further contraction by repeated additions of oxygen. What is indicated here by contraction or absence of contraction?

Likewise test the residual gas for further contraction by additions of nitrogen dioxide. What does contraction signify here? Why are observations of temperature and pressure unnecessary? (For a convenient form of record see Prob. 8, No. 65/6, Part I.)

APPLICATIONS.—Measurement of contraction, in conditions like those **47/3** just indicated, may be used to determine the real volume of oxygen or of nitrogen dioxide in a given sample—that is, the purity of the sample —provided only that there is nothing present to cause contraction in the given conditions, except these two substances. It is only necessary to make sure that the substance to be measured has been entirely used in making the observed contractions. (How is this made sure?) Then the volume of oxygen actually present may be obtained by the proportion $3:1::$ observed contraction : volume of oxygen (why?); and the volume of nitrogen dioxide may be obtained by the proportion $3:2::$ observed contraction : volume of nitrogen dioxide (why?). Apply this to determine the percentage purity of your sample of nitrogen dioxide and of oxygen. Your sample of the first will be of good quality if you reject enough to have it free from nitrogen coming from the air. Commercial oxygen is likely to be impure, also, from the presence of nitrogen.

EXPLANATORY NOTE.—The reaction by which the nitrogen dioxide **47/4** is produced is rather complicated for complete explanation at this stage; the following may suffice : The proximate (see No. 26, Part I) constituents of nitric acid are water and nitrogen pentoxide; the latter very readily gives up a portion of its oxygen to other substances, and becomes a lower oxide of nitrogen (example of multiple proportions), in this instance the dioxide; the agent which takes this oxygen from the nitrogen pentoxide is ferrous oxide, a proximate constituent of the ferrous sulphate; in thus taking oxygen this substance is converted into a higher oxide of iron—namely, ferric oxide (example of multiple proportions).

Substances which thus give up the whole or a part of their oxygen **48** are called *oxidizing agents ;* those which thus take on oxygen are called *reducing agents.*

6. The Law of Persistence or Conservation of Energy applied to Chemical Phenomena

Heat Disturbance in Chemical Reactions

(The student should read Nos. 50–55, Part I, before undertaking the experiment.)

50/1   THE UNIT OF HEAT.—The unit of quantity which is used in measuring heat is defined as the quantity of heat which raises 1 gram of water 1° in temperature, or, strictly defined, from 0° to 1° C., but, as more commonly used, from 18° to 19°. This unit is named the *calorie* (or *gram-calorie*). For convenience, a unit equal to 1,000 calories is often used, the *kilogram-calorie*, designated by the abbreviation, Cal., while for the smaller unit the abbreviation, cal., is used.

50/2   The quantity of heat disturbance is most simply measured when the reaction takes place quickly and in water solution, as in the neutralization of bases and acids. The result is commonly reckoned for the combining weights in grams of the substances used. (Recall in what reactions you have noted the liberation of heat.)

50/3   **Illustrative problem.**—To determine in calories the quantity of heat liberated in neutralizing 125 grams (its combining weight) of *oxalic* acid with ammonium hydroxide, both being in water solution.

Weigh out 5.00 grams of oxalic acid; dissolve this in 100 c.c. of water in a beaker. Take sufficient ammonium hydroxide solution to neutralize this acid,* and add enough water to bring its volume up to 100 c. c. Have the two solutions in beakers, and at a temperature not far different from that of the room. Observe carefully the temperature of each solution. Quickly pour one into the other, stir with the thermometer, and observe the resultant temperature. (The salt, ammonium oxalate, may be readily crystallized from this solution by slight concentration.)

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* The quantity will depend on the strength of the solution. It is recommended that the instructor determine this for the class, or assign it to some student as a problem.

Calculations.—In dilute solutions it may be assumed, for calculations such as these, that the quantity of heat needed to raise the solution one degree is the same as that needed to raise the water which it contains one degree.   Sometimes the weight of the water is taken, and sometimes the volume of the solution is reckoned as if it were pure water.   The latter method is somewhat the simpler.   In this experiment, the two volumes being equal, the temperature of the mixture would be the mean of the temperatures before mixing, if no heat were liberated.   The difference between this mean and the observed resultant temperature is the number of degrees that the 200 c.c., reckoned as so many cubic centimeters or grams of pure water, have been raised by the heat of the reaction.   Calculate from this the calories of heat which would be liberated by neutralizing 125 grams of oxalic acid in dilute solution.   Some heat is of course taken up by the material of the containing vessel ; how much, it would be necessary to determine, if greater accuracy were demanded.

At least two determinations should be made of this *heat of neutralization.*

CHAPTER III

COMBINING WEIGHTS—NOTATION—EQUATIONS— STOICHIOMETRY—NOMENCLATURE

No experiments.

CHAPTER IV

EXPERIMENTS ILLUSTRATING THE RELATION BETWEEN VOLUME, PRESSURE, AND TEMPERATURE OF GASES

1. The Law of Boyle

Relation between Volume and Pressure of Gases

66   Specific problem.—To investigate the relation between the volume and the pressure of a confined mass of air, its temperature remaining constant.
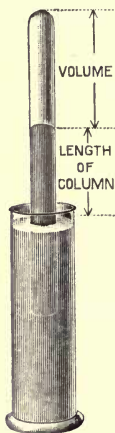
FIG. 3.—Apparatus to show Boyle's law.

Use a gasometric tube of 25 cubic centimeters in capacity, graduated in fifths (the inside must be dry), filled about one third or one half with air, the rest with mercury, and inserted, the open end down, in a narrow cylinder containing mercury. Hold the tube, using a paper holder to avoid changing the temperature by contact with the hand, in a fixed position; observe the volume occupied by the gas, reading from the top of the mercury column; measure also, the position being unchanged, the length of the mercury column from its top to the free surface of the mercury in the cylinder, using a metric rule or a common one, according to convenience. Now change the position of the tube vertically, read the new volume, and measure the new length of column. In this manner make the observations in five or six different positions of the tube.

Calculations.—It will be found convenient to record the 66/1 volumes in a vertical column, and the lengths in a column parallel with this, each corresponding horizontally with its proper volume. Deduct the several lengths of mercury column from the length of the mercury column in the barometer, and the differences thus obtained measure the relative pressures of the gas when it occupies the corresponding volumes. Now, looking for a relation between the numbers measuring volume and those measuring pressure, multiply each volume by its corresponding pressure and compare the products. (See Appendix, 15 B.)

How comes it that pressure is measured in linear units? And why is the observed pressure obtained by subtracting the observed length of column from the barometric length?

What is the limit of accuracy in your measurement of volume? Of pressure? How much variation from constancy may the products show and still prove constancy within the limits of observational accuracy? What does constancy in the products prove concerning the factors?

2. The Law of Charles

Relation between Volume and Temperature of Gases

Specific problem.—To investigate the relation between 67 the volume and the temperature of a confined mass of air, its pressure remaining constant.

Use an apparatus of the following description: A gasometric tube of 25 cubic centimeters in capacity, graduated in fifths (the inside must be dry), filled about one third or one half with air, and the rest with mercury. This is inverted, and the open end inserted in a shallow vessel containing mercury. Outside the gasometric tube is a larger glass tube, serving as a jacket, which is closed at the lower end by a stopper, through which pass centrally the gasometric tube and, either side of this, one small tube to carry steam and one to drain off the water. A thermometer is suspended beside the gasometric tube from a stopper which

loosely fits the upper end of the jacket. A flask is connected so that steam may be passed into the jacket at will, and the whole apparatus is fixed firmly in position.
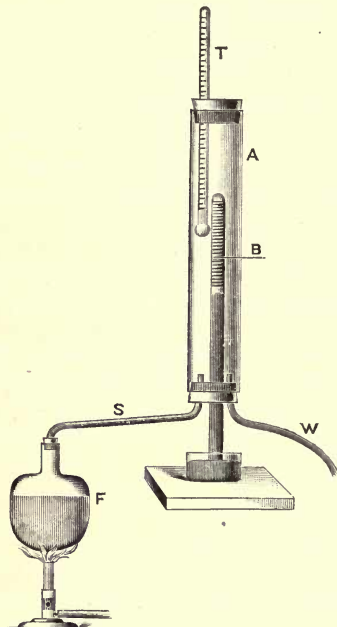
FIG. 4.—Apparatus to show Charles's law. *A*, jacket; *B*, gasometric tube containing air; *T*, thermometer; *S*, rubber tube to convey steam from the flask, *F*; *W*, tube to carry off water.

When it has stood long enough to make sure that the inclosed air has the temperature indicated by the thermometer, read the volume, pressure, and temperature. Then apply heat to the flask containing water, and pass steam into the jacket until the thermometer reaches its maximum and holds it steadily for fifteen or twenty minutes. Finally, read again the volume, pressure, and temperature. Calculate the average increase in volume for 1°, on unit volume, at the initial temperature, pressure being constant. To put this result into conventional form, so that it shall be comparable with the result as given in books, it is only necessary to assume the same rate of change between the initial temperature and 0°, that you have observed between the initial and final temperatures, and from this, to calculate the average increase in volume per degree on unit volume at 0°. This is called *the increment of volume*, also *the coefficient of expansion*.

[What would be the effect of moisture in the gasometric tube on your experimental result?]

CHAPTER V

EXPERIMENTS ILLUSTRATING THE RELATION BETWEEN EQUIVALENT AND COMBINING WEIGHTS AND CERTAIN SPECIFIC PROPERTIES

1. The Law of Gay-Lussac

Relation between Equivalent and Combining Weights of Gases, Elementary and Compound, and their Specific Gravities

Specific problem.—To determine experimentally the specific gravity (A) of oxygen, (B) of carbon dioxide, and to investigate the numerical relation between these values and the combining weights of the substances, assuming that the formula of the latter is CO_2.

[What is the specific gravity by definition? (see No. 7, Part I.) What are these combining weights, numerically?]

Assume that the weight of one liter of hydrogen at 0° and 760 millimeters is known to be 0.0899 of a gram. The experimental problem then becomes, to determine the weight of one liter of the gas in question at 0° and 760 millimeters; or, if preferred, to determine the weight of any measured volume of the gas at an observed temperature and pressure. The most direct method of solution would be to weigh a mass of the gas in a vessel of measured capacity; but the experimental difficulties in doing this make it impracticable for beginners. (Can you suggest some of the difficulties?) A less direct method is therefore followed.

71

47

A

To determine the weight of one liter of oxygen:

71/A   Use a large test-tube (about 230 millimeters or 9 inches long) fitted with a rubber stopper, carrying a glass and rubber delivery tube, like that of the gas generator. The test-tube must be thoroughly dry.

Weigh out roughly about 5 grams of manganese dioxide (symbol MnO_2). Place this in the porcelain crucible and ignite it with the full heat of the flame for ten or fifteen minutes to insure complete dryness.

Weigh out roughly about 20 grams of powdered potassium chlorate (symbol $KClO_3$). Mix the two substances thoroughly in a clean mortar; transfer to the test-tube, and wipe any adhering dust from the upper part of the tube. Insert, to lie just back of the stopper, a loose plug about 15 millimeters (one half inch) wide, made of a coiled strip of asbestos board or of glass wool.

Weigh carefully, to hundredths, the tube and contents thus prepared.

Support the tube horizontally between two rings of the iron stand, and tap it gently so that the powder shall lie somewhat spread out. Insert the stopper and connect with the large collecting bottle in the tank.

Recall the experiment (No. 41/₃ c) with hydrogen under Law 4, Chapter II, and follow here the details of manipulation there directed for the collection and measurement of the gas generated.

Heat the mixture gently so as to avoid too rapid evolution of gas. It is best to apply heat to only a small portion of the mixture at a time, for, if the whole mass becomes heated, the evolution of gas will not cease when the flame is withdrawn, and more than the bottleful may be generated. When nearly sufficient gas to fill the bottle has been collected, withdraw the heat, and when bubbles cease to pass, remove the stopper, lest water be drawn into the

tube; let the tube cool, and carefully weigh it. The loss in weight is taken as the weight of the oxygen which has passed out of the tube.

The volume of this gas is measured in the collecting bottle, as before indicated. It is well to shake the gas with the water remaining in the bottle, and then to reopen the bottle for a second under water. (Why?)

Calculations.—From this weight and this volume calcu- 71/1 late the weight of one liter of oxygen at 0° and 760 milli-meters, and from this value calculate the specific gravity of the gas and compare it with its combining weight.

Make a second determination of the same. The original charge will be more than sufficient to generate two bottlefuls.

Secondary observation.—After the second determination, 71/2 collect some of the gas in a small bottle and test it with a lighted match. (See Appendix, 19, I and IV.)

EXPLANATORY NOTE—The potassium chlorate, symbol $KClO_3$, by heating loses its oxygen and becomes potassium chloride, symbol KCl. The temperature at which this decomposition takes place is lowered by the presence of the manganese dioxide, hence its use.

B. First Step

To determine the weight of the carbon dioxide gener-ated from a weighed quantity of calcium carbonate by the action of an acid:

Weigh out with care 5.00 grams of this substance in pow- 81/1 der. Transfer it without loss to a filter paper, wiping off any dust adhering to the glass crystal with a small piece of paper. Wrap the whole in a small package, and put it in a beaker. Weigh this beaker with its contents.

In a second beaker put about 20 grams (15 c. c.) of nitric acid and a glass rod, and weigh this beaker with its contents. Cautiously pour acid from the second beaker into the first, a little at a time, until there is no further action. Then weigh

again each beaker and its contents. The loss of weight in the system is taken as the weight of carbon dioxide generated. Make at least two determinations of this quantity.

B. Second Step

To determine the volume of the gas generated by the action of an acid on a weighed quantity of calcium carbonate :

81/2   Weigh out 10.00 grams of the calcium carbonate, wrap in a paper as in No. 81/1, and transfer without loss to the gas generator. Now, carbon dioxide, being soluble in water, can not be collected over water without loss. The difficulty is avoided by using an intermediate bottle, holding about four times as much as the collecting bottle. It is provided with a two-holed stopper, through one hole of which passes a bent glass tube, terminating close to the bottom of the bottle ; through the second hole passes a tube terminating just below the stopper, and to the outer end of this is attached a rubber tube carrying the delivery tube. The delivery tube of the generator is now connected with the first tube of the large bottle, and the delivery tube of the latter is inserted in the mouth of the collecting bottle. The gas from the generator will thus be passed to the bottom of the large bottle and, being considerably heavier than air, will lie there some little time, while an equal volume of air will pass out from the top and may be collected and measured, as in the hydrogen experiment. After the connections are made the apparatus should be tested for leakage (see Exp. 41/3 b).

Pour about 40 grams (30 c. c.) of nitric acid, a little at a time, through the thistle-tube until the reaction ceases. Note the volume of the acid used (why ?), the temperature of the water in the tank, that of the room, and the height of the barometer. Make thus at least two determinations of the volume of gas generated.

Calculations.—From these observations calculate first 81/3 the weight of one liter of the gas at 0° and 760 millimeters, then the specific gravity referred to hydrogen, and finally the ratio of the specific gravity to the combining weight.

Note.—The intermediate bottle, after once serving, 81/4 before being again used, must be cleaned of its gas. This may be done by blowing it out with a pair of bellows, the nozzle of which, extended by a rubber tube, reaches to the bottom of the bottle.

Explanatory Note.—In this reaction the factors are calcium car- 81/5 bonate (a salt) and nitric acid; the products are calcium nitrate (a soluble salt), water, and carbon dioxide, the latter appearing as a gas. This may be expressed by equation, thus:

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

calc.	nitric	calc.	water.	carbon
carb.	acid.	nitrate.		dioxide.
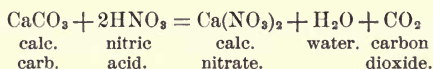
Recall the similar reaction in the experiment under Law 1, Chapter II (No. 36).

2. The Law of Dulong and Petit

Relation between Equivalent and Combining Weights of Elementary Solids and their Specific Heats

Definition of specific heat.—The specific heat of a sub- 95 stance is the quantity of heat required to raise in temperature 1 gram of the substance 1°, divided by the quantity of heat required to raise 1 gram of water 1°.

It is necessary to discriminate carefully between quantity of heat and temperature. The unit of quantity (see No. 50/₁) is called the *gram-calorie*, and is the quantity of heat required to raise one gram of water one degree (strictly from 0° to 1°, practically from 19° to 20° or thereabouts). Therefore specific heat may better be defined as the quantity of heat, measured in gram-calories, required to raise one gram of the substance one degree.

95/1   **Specific problem.**—To determine experimentally the specific heat, and to investigate the numerical relation between this value and the combining weight in the case (A) of lead, (B) of zinc, (C) of tin.*

A

95/2   **Specific heat of lead.**—Weigh out carefully 100.0 grams of lead (shot), transfer it to a large dry test-tube, set the tube and contents in water contained in a suitable vessel, and boil the water. The lead should be immersed below the surface of the water.

Weigh out carefully in a beaker 50.0 grams of water which has the temperature of the room; test with the thermometer to see that the temperature does not change in an interval of five minutes. Put the thermometer, first drying it, in the lead, and see that it reaches a maximum which it holds for at least five minutes. Record this temperature. Then put the thermometer back in the water, stir, read the temperature carefully, and record it.

Now, as quickly as possible, take the test-tube from the water, pour the warm lead into the water which the beaker contains, stir gently with the thermometer, quickly read the maximum temperature and record it.

The observations therefore are: The weight of the water and its temperature just before mixing; the weight of the lead and its temperature just before mixing; the temperature of the resultant mixture.

95/3   **Calculations.**—Let

$x =$ the quantity of heat required to raise 1 gram of lead 1°;
$y =$ the quantity of heat required to raise 1 gram of water 1°;
$t =$ the degrees of temperature lost by the lead;
$t' =$ the degrees of temperature gained by the water.

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* One of these three determinations may be thought sufficient, or perhaps all may be omitted if the student has already made similar ones in physics.

It follows that

$100 \times t \times x =$ the quantity of heat lost by 100 grams of lead in cooling $t°$.

$50 \times t' \times y =$ the quantity of heat gained by 50 grams of water in warming $t'°$.

If now the experimental conditions are made such that the lead shall lose no heat save what goes to the water, and the water gain no heat save what comes from the lead, then these two quantities of heat must be equal. Equating the two expressions gives

$$100 \times t \times x = 50 \times t' \times y.$$

From which is obtained

$$\frac{x}{y} = \frac{50 \times t'}{100 \times t} = \text{Specific heat by definition.}$$

The experimental conditions called for to justify this equation can be but crudely realized by the directions here given, but sufficiently to give a good illustration of method. Calculate the quantity of heat required to raise 205 grams of lead 1°.

B

Specific heat of zinc.—Weigh out carefully 50.0 grams of 95/4 granulated zinc, and 50.0 grams of water. The procedure and calculations are the same as in the case of lead. Calculate the quantity of heat required to raise 65 grams of zinc 1°.

C

Specific heat of tin.—Use 50.0 grams of tin in coarse 95/5 powder, and 50.0 grams of water, and proceed as in B. Calculate the quantity of heat required to raise 118 grams of tin 1°.

NOTE.—Save the material used in these experiments, so that it may be dried and be ready for use again.

21

3. The Law of Mitscherlich

Relation between Composition, and hence Combining Weight, and Specific, i. e., Crystalline Form

107   No experiments.

4. The Law of Raoult (I)

Relation between Combining Weights of Solutes and Specific Depressions of the Freezing Point in Specified Solvent (See Part I, Nos. 21 and 23/₁)

111   **Specific problem.**—I. To investigate experimentally the relation between the depression of the freezing point and the quantity of the solute (A) when the solute is camphor and the solvent paraffin; and (B) when the solute is naphthalene and the solvent paraffin.

II. To investigate the numerical relation between the specific depression (i. e., depression for 1 gram of solute in 100 grams of solvent) of camphor in paraffin, and of naphthalene in paraffin, and the combining weights of the solutes.

A

111/1   (1) Weigh out carefully 10.00 grams of paraffin and 0.80 of a gram of camphor. Melt the paraffin in an evaporating dish on the water-bath, then add the camphor and let it dissolve, stirring well. Pour a suitable portion of the solution into a clean, dry test-tube. Let the liquid be about one inch deep. In another tube put some paraffin. Have a stirring-rod in each tube, and attach the tubes by rubber bands to a thermometer. Suspend the tubes in a beaker containing water, so that they are suitably immersed, and apply heat until the mixture melts. Allow to cool very slowly, keeping the mixtures and the water well stirred, and observe the freezing points. Repeat several times for constant results. It will save time to prepare the solution

called for in Exp. 111/₂, and to attach the three tubes at one time to the thermometer.

(2) Make a mixture of 10.00 grams of paraffin and 1.20 **111/2** grams of camphor, as in (1), and in a similar manner determine its freezing point. Are the depressions approximately proportional to the quantities of the solute in a constant quantity of the solvent?

Calculate the specific depressions—i. e., depressions for 1 gram of solute in 100 grams of solvent—and take their average.

B

(3) Make a mixture of 10.00 grams of paraffin and 0.60 **111/3** of a gram of naphthalene, as in A; (4) also of 10.00 grams **111/4** of paraffin and 1.20 grams of naphthalene. Observe the freezing points, and make the calculations as before.

II. Multiply the specific depressions of camphor in **111/5** paraffin by the combining weight of camphor ($C_{10}H_{16}O = 151$), and the specific depression of naphthalene by the combining weight of naphthalene ($C_{10}H_8 = 127$), and compare the products. Are they approximately constant?

NOTE.—It will be realized that the probable error of reading on the **111/6** ordinary thermometer is so large a fraction of the depression itself, that the results can not be quantitatively very satisfactory. A thermometer reading at least to hundredths would be needed for good results. Calculate the variation in the product made by the variation of one quarter of a degree in the depression.

NOTE.—The tubes may be cleaned by immersing in boiling water, **111/7** and the dishes by wiping with filter paper while still warm.

5. The Law of Raoult (II)

Relation between Combining Weights of Solutes and Specific Elevations of Boiling Temperature in Specified Solvent (See Part I, Nos. 21 and 24/₄)

Specific problem.—I. To investigate experimentally the **127** relation between the elevation of the boiling temperature

and the quantity of the solute (A) when the solute is sodium acetate and the solvent water, and (B) when the solute is potassium tartrate and the solvent water.

II. To investigate the numerical relation between the specific elevation of boiling temperature—i. e., elevation for 1 gram of solute in 100 grams of solvent—by sodium acetate in water, and by potassium tartrate in water, and the combining weights of the solutes.

A

127/1   (1) Use a small distilling flask, as in the observation of boiling point (see Appendix, 17). Put in it a suitable quantity of water and some bits of pumice (why the latter? See No. 24/₂, Part I), boil, and observe carefully the temperature of the boiling water. Repeat all readings for constant results.

127/2   (2) Drain the water thoroughly from the flask, and put in its place a solution of 100.0 grams (or 100 cubic centimeters) of water and 15.00 grams of sodium acetate with clean pumice. Again observe the temperature of the boiling solution.

127/3   (3) In a similar manner observe the boiling temperature of a solution containing 100.0 grams (or 100 cubic centimeters) of water and 30.00 grams of sodium acetate.

Are the elevations approximately proportional to the quantities of the solute in a constant quantity of the solvent? Calculate the specific elevations, and take their average.

B

127/4   (4) Observe the boiling temperature of a solution of 100.0 grams (or 100 cubic centimeters) of water and 20.00 **127/5** grams of potassium tartrate ; (5) also of 100.0 grams (or 100 cubic centimeters) of water and 40.00 grams of potassium tartrate. Make the same calculations as before.

II. Multiply the specific elevation of sodium acetate 127/6
($NaC_2H_3O_2$) in water by the combining weight of the same, and the specific elevation of potassium tartrate ($K_2C_4H_4O_6$) by its combining weight, and compare the products. Are they approximately constant?

The same remark as to accuracy of observation applies here as under the preceding law. Care should be taken that the bulb of the thermometer is completely immersed in the liquid.

NOTE.—The solutions may be saved in order to recover the salts by crystallization.

Alternative experiment.—Instead of the solutions indi- 127/7
cated in the preceding experiment, may be used the follow-
ing : A 15.40 per cent and a 30.80 per cent solution of potas-
sium chloride (KCl), and an 11.00 per cent and a 22.00 per
cent solution of ammonium chloride (NH_4Cl).

EXPERIMENTS ILLUSTRATING THE METHOD OF DETER-MINING EQUIVALENT AND COMBINING WEIGHTS OF ELEMENTS AND FORMULAS OF COMPOUNDS

1. Determination of the Equivalent Weight of an Element

144 **Specific problem.**—To determine experimentally the mass of tin which combines with 7.94 grams of oxygen. (Tin does not combine with hydrogen.)

144/1 EXPLANATORY NOTE.—It is not practicable to cause a weighed quantity of tin to combine with oxygen of the air, and to weigh the oxide obtained ; but by the action of nitric acid, the oxidizing power of which has already been noted [in what connection?], an oxide of tin is produced which does not volatilize, does not combine with nitric acid, and does combine with water, forming a compound, however, from which the water is expelled by prolonged heating, leaving simply the oxide. The excess of nitric acid is also volatilized by heat.

144 Weigh very carefully to hundredths of a gram a small evaporating dish, clean and dry, together with a short glass rod.

Weigh out carefully 5.00 grams of pure tin foil. Put a portion of this in small pieces in the evaporating dish, and just moisten with nitric acid. When the action is nearly over, put in more tin, and then moisten again with acid. Continue this until all the tin is used, with the minimum of acid that will suffice.

Describe what takes place. What is the brown gas produced ? Have care not to inhale it ; it is well to use the hood. Also bear in mind the extreme corrosiveness of nitric acid. Use the rod to pour by, leaving it in the dish. Keep the outside of the beaker clean. Have a wet sponge at hand.

Heat the dish and contents on the water-bath until the liquid has entirely volatilized, transfer to the iron ring of the stand, apply the direct flame, gently at first passing it back and forth, then give it the full heat of the burner, continuing for some time after the fumes have ceased to appear. The powder should be slightly brown when hot, and yellowish when cool.

Let the dish become thoroughly cool, and weigh it with its contents to hundredths of a gram. To insure the completeness of the operation, ignite again for fifteen or twenty minutes, let cool, and weigh again.

Assuming that you have in the dish a compound containing only tin and oxygen, calculate the weight of oxygen which has combined with the 5 grams of tin, and from this the weight of tin which combines with 7.94 grams of oxygen. Make at least two complete determinations. **144/2**

2. Determination of the Combining Weight of an Element

Under the law of Dulong and Petit choose what multiple of the equivalent weight determined in No. 144/$_2$ shall be taken as the combining weight of tin. The specific heat of tin is 0.056. (See Nos. 101 and 105, Part I.) **150**

It will be realized that the utmost care must be taken in the manipulation, since the weighings must be to hundredths of a gram, and the variation in the quantity of oxygen for 5 grams of tin should not be more than one or two hundredths of a gram. **150/1**

Having determined the combining weight of tin, deduce the formula for the oxide. Try to write the equation for the reaction between tin (symbol, Sn) and nitric acid, HNO_3. What is the percentage of tin and of oxygen in tin oxide? **150/2**

3. Determination of the Formula of a Compound

Specific problem.—To determine the percentage of the proximate constituents, carbon dioxide, CO_2, and sodium **154**

oxide, Na_2O, in the compound, sodium carbonate, and from these to deduce the formula of the compound.

154/a   (a) To determine the percentage of carbon dioxide: Take a sufficient quantity of the sodium carbonate for all the following experiments, heat in the larger evaporating dish over the flame, gently and not too hot.   This is simply to secure the dryness of the sample.

Weigh out carefully 5.00 grams of the dry sample, and follow the procedure given for determining the weight of carbon dioxide in calcium carbonate (see Exp. 81/1), using hydrochloric instead of nitric acid.   Make at least two determinations.

Calculate the result as grams of carbon dioxide in 100 grams of the sample.

Secondary observation.—Filter and crystallize the salt which is left in solution.   What substance is it?

(b) To determine the percentage of sodium oxide:

154/1   EXPLANATORY NOTE.—Since it is not practicable to separate this constituent from the compound, and weigh it by itself, it is necessary to convert it quantitatively into some substance which it is practicable to separate and weigh, and the composition of which is known.   For this purpose the carbonate is converted into sodium nitrate by the action of nitric acid, the carbon dioxide escapes, and the water and excess of nitric acid are volatilized.   Sodium nitrate is not volatile, and is not decomposed by heating short of fusion.   Its composition is given by the formula $Na_2N_2O_6$, or, as usually expressed, $NaNO_3$.   [What percentage of Na_2O does this formula show?]

154/b   Weigh out carefully 5.00 grams of the dry sample of sodium carbonate in a small evaporating dish, the weight of which has been determined to hundredths of a gram. Neutralize this with nitric acid, using a very slight excess, and having care not to lose by effervescence.   Evaporate on the water-bath until the liquid has disappeared, and then, passing the burner back and forth, heat gently until the substance just begins to melt.   Let cool, and weigh. The substance obtained is sodium nitrate.   Make thus at

least two determinations of the weight of this substance obtained from 5 grams of the carbonate.

Knowing the percentage of sodium oxide in sodium nitrate, calculate the weight of sodium oxide contained in the weight of the nitrate obtained, and reckon this result as grams of the oxide in 100 grams of the carbonate.

Secondary observation.—Redissolve and crystallize the sodium nitrate.

(*c*) To deduce the formula :

Since the proximate constituents are carbon dioxide, **155** CO_2, and sodium oxide, Na_2O, the formula must be $(Na_2O)_x$ $(CO_2)_y$, the coefficients, x and y, to be deduced from the percentages experimentally obtained. Hence divide the percentage of each constituent by the combining weight of the same, and the quotients give the ratio of the coefficients, x and y. Now these quotients are not necessarily whole numbers, but the peculiarity of chemical phenomena is that they stand in the ratio of whole numbers, usually quite small. Hence inspection or division by the smallest will suffice to show the smallest whole numbers that have the ratio of the quotients. In this specific problem the approach of the quotients to equality measures the accuracy of the experimental work. The simplest values, therefore, for x and y are 1 and 1, and, in the properties of this substance, no reason is found for using any multiples of these values. The accepted formula is therefore $Na_2O \cdot CO_2$, or, as it may also be written, Na_2CO_3.

[Write the equation for the reaction between sodium carbonate and nitric acid.]

CHAPTER VII

THE ATOMIC THEORY

No experiments.

CHAPTER VIII

RELATION BETWEEN THE PROPERTIES OF THE ELEMENTS IN GENERAL AND THEIR COMBINING WEIGHTS

Experimental Study of the Properties of the First Twenty-five Elements (in the Order of their Combining Weights) and Some of their Compounds

So far as practicable, each element in turn will be presented in its free condition for descriptive study : first as to its physical properties, those which appear on inspection, and others ; second, as to its chemical properties. Then will follow the study of some of its most important compounds. It is judged unnecessary to give detailed directions for manipulation in all experiments, as by this time the student should have had sufficient experience in the laboratory to give him some judgment of his own as to how to do things. Some of the manipulations, too, are repeated many times.

1. HYDROGEN

Symbol H.—Comb. wt. 1

202   **Preparation.**—See Exps. $17/_1$ and $41/_4$ and Appendix, 19, I. Use the small collecting bottles or test-tubes. Use iron (nails) or zinc and hydrochloric or dilute sulphuric acid.

NOTE.—*Hydrogen with air makes a mixture which may explode dangerously on ignition. Therefore the greatest*

caution must always be taken to avoid accident from unexpected ignition by contact with flame.

Physical Properties

Observe as to *color, odor* (any odor is due to impurity). **203**
As to weight compared with air.—A crude test: Fill a test-tube with hydrogen over water, close with the thumb, hold its mouth downward directly over and close to the mouth of a second tube, then remove the thumb quickly, bringing the two ends together, reverse the position of the tubes, separate them, closing the second, now the upper one, with the thumb, and test at the flame for the presence of hydrogen in both tubes.

As to solubility in water.—A crude test: Collect in a **204** test-tube, leaving a little water; close tightly with the thumb, shake, open under water, close, and shake again. Repeat this several times, and note if the volume of water in the tube increases and the gas decreases.

As to relative diffusibility.—Use a dry glass tube, closed **203/1** at one end with a porous plug of plaster of Paris, and open at the other. Close temporarily the plugged end with the thumb or a cork, and fill the tube thoroughly by dry displacement—i. e., hold the tube open end downward, thrust the delivery tube at first well up to the top, then slowly withdraw it (compare Appendix, 19, VI). When the tube is full, immerse the lower, open end in water, uncover the porous plug, and allow to stand for some time. What takes place? Can you explain the phenomenon?

A modification of the preceding experiment, suitable to be performed **203/2** by the teacher before the class: Use a porous battery jar, closed by a cork or a plaster plug through which passes a glass tube of convenient length. Support this so that the lower open end of the tube is immersed in a colored liquid (e. g., water, colored by potassium permanganate). Slowly lower over the porous jar a glass bell jar filled with hydrogen. When the gas ceases to bubble from the end of the tube, remove the bell jar. The same may be tried with illuminating gas in place of hydrogen.

205   **Occlusion.**—Hold a piece of platinum sponge (i. e., finely divided platinum deposited on the surface of asbestos fiber), thoroughly dried, in the stream of hydrogen issuing from the delivery tube, but only when the gas is sufficiently pure to be ignited with safety.

[This experiment, like the preceding one, may best be performed by the teacher.]

Chemical Properties

Test as to the action of hydrogen on wet litmus paper.

207   **Test as to combustibility.**—With suitable precaution, the gas issuing from the delivery tube may be ignited as a jet, but, owing to the danger of explosion, this should not be tried until the action has continued long enough to expel the air from the generator. It is best always to test a small sample of the gas thus: Collect in a test-tube over water, close with the thumb, bring it to the flame, mouth downward, remove the thumb, ignite the gas, and slowly invert the tube. The gas should burn quietly in the tube. If it burns quickly with a slight report, it is not safe to ignite at the generator.

207/1   *Make it a rule always to wrap several folds of the towel over and around the generator before igniting the gas, no matter how confident you may be of its purity. Serious accident may follow neglect of this precaution.*

Observe the character of the hydrogen flame; hold a dry glass plate or beaker over the flame. What is the product of combustion?

208   **Nascent state.**—Use four test-tubes, fill about two thirds full with water, and color each portion slightly with a few drops of potassium permanganate solution. Into the first put a few fragments of zinc and a few drops of sulphuric acid, and let the action continue for some minutes. What is the result? What substance is it which causes the color to disappear? To answer this, place in the second tube some zinc, in the third some sulphuric acid, and into the fourth let the hydrogen from the generator slowly bubble, preferably using zinc as the metal.

EXPLANATORY NOTE.—The permanganate loses its color in conse- **208/1** quence of losing some of its oxygen. The oxygen is taken from it by the hydrogen, but only at the moment of its liberation from the acid, when it is said to be in the *nascent state*. The experiment may not be entirely satisfactory, for the reason that the impurity which is usually carried by the hydrogen from the generator, and which comes from the metal, and imparts the odor to the gas, tends to remove oxygen from the permanganate. Observe as to the odor of the gas which has bubbled through the colored liquid.

To explain the phenomenon of the nascent state it has been sug- **208/2** gested that the substance in the atomic condition may show an activity which is wholly or partly lost after the atoms have come together into molecules.

Another method of generating hydrogen.—Use a few frag- **202/3** ments of zinc in a test-tube with a dilute solution of sodium hydroxide. The reaction is facilitated by a piece of iron (a nail) in contact with the zinc.

2. LITHIUM

Li.—6.97

No experiments, unless to show a sample of some **210** salt of lithium—e. g., the chloride—and the color it imparts to the flame.

3. GLUCINUM or BERYLLIUM

Gl. or Be.—9.0

No experiments. **216**

4. BORON

B.—10.86

Boron is difficult of preparation, so it is impracticable to show it. It forms an oxide whose symbol is B_2O_3, and which combines with water, forming boric acid. The sodium salt of this is the familiar commercial substance, borax.

Borax and boric acid crystallized.—Saturate about a **225** beakerful of water with borax. Filter, if not clear, and

set aside about one half of this to crystallize. To the remainder add about one half its volume of hydrochloric acid, and set this aside to crystallize. Observe the different appearance of the two substances when crystallized.

Rinse a sample of each substance quickly with a very little cold water, and dry it on filter paper. Observe the reactions on litmus paper.

226   **Flame coloration.**—Put a very small quantity of borax in an evaporating dish, add a few drops of alcohol, ignite the alcohol, and observe the color of the flame, while stirring the mixture. Extinguish the flame, add a few drops of dilute sulphuric acid, reignite the alcohol, and again observe the flame color. This test is often used to recognize boric acid and its compounds.

228   **The borax bead.**—Melted borax has the property of dissolving many metallic oxides, and these often impart characteristic colors to the substance. This test is very useful in qualitative analysis. To make a borax bead, use a piece of platinum wire, about 75 millimeters (3 inches) long, one end of which is fused into a piece of glass tubing for a handle. Bend the free end of the wire around the sharpened end of a lead pencil, so as to make a small loop. Heat this red hot, touch it to some powdered borax, and heat the borax which adheres to the wire. What is the first effect of this, and to what is it due? (see Exp. 21/$_7$.) When the borax has fused to a clear, glasslike bead, touch it, while still hot, to some particles of copper oxide. These adhere to the hot bead. Do not let it take up too much—a very minute quantity suffices; and if you have not enough on first trial, it is easy to add more, but it is not so easy to reduce the quantity. Heat again to fuse the bead with the adhering copper oxide. The particles of the latter can be seen slowly to dissolve, often with beautiful play of colors on the surface of the bead. Observe the color of the bead, when hot, and when cold. The bead should be transparent, but, if too much material has been put in, it

will be opaque, so the color can not be distinguished. In
this event, clean the wire, leaving only a fragment of the
bead, and add more borax. To clean the wire, heat the **229**
bead hot, and quickly cool it in water. This makes the
mixture brittle, so that it can be easily removed. To get
the best results, in the bead experiments, the mouth blow-
pipe should be used for heating. By this means the char-
acter of the flame can be so varied as to cause the oxida-
tion of the dissolved substance, or the removal of oxygen
from it—i. e., reduction. These changes often produce
changes in color. Thus the copper bead is blue when
heated in the oxidizing flame, and it has the color of metal-
lic copper in the reducing flame. (Concerning the use of
the blowpipe see Appendix 21.)

Manganese in the bead.—After seeing the color of the **228/2**
copper bead in the oxidizing and in the reducing flame,
make a new bead and color it with manganese dioxide. Ob-
serve the color in each flame.

5. CARBON

C.—11.91

Elementary carbon exists in three allotropic forms, **234**
diamond, graphite, and charcoal; only the last is here
studied.

Preparation.—Heat a small quantity of sugar on the **248**
spatula blade. It burns and chars. The black charred
material consists mainly of carbon. In similar manner
many other substances show the charring effect of heat,
and this is evidence of the presence of carbon as a con-
stituent in the substance. It is due to the removal in part
of other constituents, particularly hydrogen, by combustion,
the less easily combustible carbon being left as residue.

Place some fine shavings in a dry test-tube, fitted with **254**
a cork and a short glass delivery tube, and apply the full
heat of the flame. Note the appearance of moisture and

white fumes.   Ignite the gas issuing from the tube.   After the heating observe the black residue in the tube.   This is charcoal.   Note also the liquid, having tarry odor.   Test it with litmus.

The application of heat in this manner, without free access of oxygen or air, is called *dry* or *destructive distillation*.   It is applied on a large scale to the production of various substances from wood, and likewise to the production of illuminating gas and other substances by the de-

253 structive distillation of coal.   Heat a little soft coal in a test-tube, as in No. 254.

Properties of Carbon (Charcoal)

254/1   **Porosity.**—Holding a piece of charcoal in the tongs, plunge it beneath the surface of some hot water.   Is charcoal heavier or lighter than water?   Keep it under hot water for a considerable time.   Does it finally sink in the water?

255   **Absorptive power.**—Generate a very little hydrogen sulphide, using a piece of iron sulphide not larger than a bean and a few drops of hydrochloric acid, and collecting the gas in a dry bottle covered with a glass plate (Appendix, 19, V).   Drop into this a piece of charcoal, previously heated for a few seconds in the gas flame.   Set this aside with the cover on, and some time later observe by odor if the gas has been absorbed by the charcoal.

255/1   In a beaker containing water, colored by a few drops of potassium permanganate solution, place a small quantity of boneblack (animal charcoal), boil for a few minutes, then filter.   Does the filtrate lose its color?   Is the color removed by filtering simply, without the use of the charcoal?

257   **Combustion.**—Does the substance burn?   Does it burn with a flame?   Why not?

257/1   **Product of combustion.**—Ignite a piece of charcoal in the flame until it is well aglow, then drop it into a bottle and cover the latter with a glass plate.   When the coal is ex-

tinguished, either take out the remaining charcoal or invert the bottle over another bottle, pouring thus the heavy gas from the first into the second bottle and leaving the charcoal. Next pour into the second bottle some lime-water (calcium hydroxide solution, CaO_2H_2) and shake the contents. The white precipitate is calcium carbonate, $CaCO_3$, and its formation may generally be taken as evidence of carbon dioxide, which is, in fact, the combustion product of carbon. Write the equation for the formation thus of calcium carbonate.

Reducing power.—Make a shallow hole in a piece of **257/2** charcoal, place in this a small quantity of litharge (lead oxide), and turn the flame (reducing) of the blowpipe upon this (see Appendix, 21, II). Describe and explain what takes place.

5a. *Carbon Dioxide, CO_2*

Preparation.—Use calcium carbonate and hydrochloric **261** acid in the generator. Collect the gas by upward displacement of air (Appendix, 19, V) in the small collecting bottles.

As to solubility.—Test as in Exp. 204.   **262**

As to combustion and specific gravity.—Plunge the lighted **263** taper slowly into a bottle filled with the gas.

Place the lighted taper in one bottle, and pour upon it the heavy gas from a second bottle. Holding a piece of magnesium ribbon in the tongs, ignite it at the flame and plunge it into a bottle well filled with the gas. What is the white powder seen in the bottle after this experiment? What is the black substance? Why does it retain somewhat the form of the ribbon?

As to acid reaction.—Test the action on wet blue litmus **264** paper.

As to reaction with lime-water (calcium hydroxide solu- **265** tion).—Collect some of the gas in a test-tube, pour in some lime-water, and shake. Pass in repeatedly more of the gas

22

until the precipitate at first formed nearly or quite disappears. Then boil the contents of the tube. Explain the reprecipitation.

265/1   EXPLANATORY NOTE.—Excess of carbon dioxide in water forms with calcium carbonate an acid carbonate which is soluble in water. This compound is broken up at the temperature of boiling and the excess of carbon dioxide is expelled, in consequence of which the insoluble calcium carbonate reappears. Many natural waters contain this acid carbonate of calcium or of other bases, and therefore become turbid and deposit sediment by boiling. Test some sample of natural water for this effect. See also Part I, No. 271.

267   **Carbon dioxide in the breath.**—Through a glass tube blow air from the lungs into some li ie-water.

5d. *The Hydrocarbons*

Methane, CH_4

276   **Preparation.**—Take about equal bulks of lime, CaO, and of sodium acetate, $NaC_2H_3O_2$; pulverize and mix them thoroughly in the mortar; put some of the mixture in a dry test-tube (about three quarters full), which is provided with a cork and delivery tube; support this on the iron ring, heat, and collect the gas over water in test-tubes.

277   **Properties.**—Examine the gas as to color, odor, solubility in water, and action on litmus (after the sample of gas has been shaken with water). Test for combustibility by igniting a test-tubeful at the flame; then test for a product of combustion by pouring some lime-water into the tube in which the gas has quietly burned, and shaking. What are the products of combustion? The combustibility may be tested also by igniting the gas at the end of the delivery tube.

Acetylene, C_2H_2

280   **Preparation.**—Put three or four lumps of calcium carbide, CaC_2, in the gas generator, with enough alcohol to cover the end of the thistle-tube. Add water through the

thistle-tube, a few drops at a time, so as to regulate the flow of gas, and collect the gas over water in test-tubes as for methane.

Properties.—Examine as to color, odor, solubility in **281** water, and action on litmus, as with methane. Test as to combustibility by igniting a test-tubeful of the gas at the flame, then mix air with acetylene in a test-tube and ignite. Do *not* try to ignite the gas at the delivery tube without the precautions taken with hydrogen (testing a small sample and throwing the towel over the generator), for *a mixture of acetylene and air may be very explosive.*

Describe what takes place in the generator, also the appearance of **281/a** calcium carbide. Is the latter combustible? Allow a lump of it to lie exposed to the air for twenty-four hours. Is it deliquescent? Is it hygroscopic? Test the liquid left in the generator with pink litmus. The reaction in the generator is thus expressed :

$$CaC_2 + H_2O = C_2H_2 + CaO.$$
$$CaO + H_2O = CaO_2H_2 \text{ (calcium hydroxide)}.$$
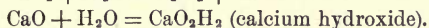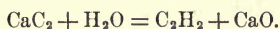
5e. *Flame*

Flame is simply gas, burning freely. A non-volatile **284** combustible like carbon burns without flame. To observe some of the characteristics of flame, use the Bunsen burner, turned low, and the air shut off. Note the three different portions of the flame : First, the outer cone, pale blue, visible only at the base of the cone, where the light is feeble; second, the bright luminous cone ; third, the dark interior cone. In the *outer cone* the combustion is complete, since there is free access of air. In the *middle luminous cone* the combustion is incomplete, since the air does not penetrate so far ; but the temperature is high, and under these conditions the carbon-containing constituents of the gas undergo chemical change somewhat as seen in the destructive distillation of wood. This results in the separation of more or less carbon as very small solid particles. These are raised to a high temperature, white heat (incandescence),

before they come to the outer cone, where they burn to carbon dioxide.

285   Hold a cold object, like a porcelain dish, in this flame, and some of the carbon is deposited thereon (as soot) before it can reach the air and burn.

286   The *inner dark cone* contains unburned combustible gas, and the temperature is much lower. Insert the open end of a narrow glass tube in this cone, and the unburned gas may be drawn off and ignited at the upper end of the tube. Quickly thrust the head of a match through the outer cones and into the inner one. It does not take fire while held there, since the temperature is comparatively low and there is no air; but the wood of the match quickly burns at the edge of the flame. A piece of wire thrust horizontally through the flame is seen to become luminous first where it cuts the outer cones, while the portion in the inner cone remains dark for a few seconds.

287   With a few trials, a card, or a sheet of stiff paper may be lowered directly down upon the flame and quickly removed without taking fire, but it will show a ring of scorching where it has cut the outer cones. Lower a piece of wire gauze down upon the flame, and the dark central portion and the luminous ring are plainly seen.

288   In this experiment with the gauze it is seen that, although the gas is free to pass through the gauze, the flame is only on the lower side of it. The gas above the gauze may be reignited with a match.

Bring the gauze squarely down upon the flame quite to the burner, and the flame may thus be completely extinguished. Or, thrust the gauze through the flame horizontally and close to the burner so that there is no flame underneath it, then raise it to the tip of the cone, and the flame is likewise extinguished.

289   These effects are due to the fact that the gauze, being a good conductor of heat, reduces the temperature of the gas below its point of ignition. A valuable application of the fact is seen in the safety lamp,

invented by Sir Humphry Davy, which miners carry in coal mines where there are combustible gases and where there is consequently danger of explosive ignition by the lamp. The lamps are inclosed by a chimney of wire gauze which permits air to pass in, but no flame to pass outward.

Effect of temperature on luminosity.—The fact that the **290** lowering of temperature lowers also the luminosity of flame may be seen by bringing against the flame a porcelain dish, or, better, an iron plate. The bright portion almost disappears, and hardly more than the pale blue is seen.

The Bunsen flame.—By opening the valves at the base of **291** the chimney, so that air enters and mingles with the gas before it burns, the character of the flame is greatly changed. The presence of air in the interior of the flame brings about more complete combustion, the solid particles of carbon do not separate, luminosity nearly disappears, and no soot is deposited on cold objects. The luminosity may be momentarily restored by blowing any fine dust into the flame, such as iron dust, charcoal, or sodium carbonate.

The reduction of luminosity is not dependent on com- **292** plete or increased combustion, since a gas containing no oxygen, such as nitrogen, produces the effect, if mixed with the gas before burning. In this case dilution and consequent reduction of temperature probably bring about the result.

Recall in this connection the character of the flame made by the use of the mouth blowpipe. (See No. 229, Part II, and Appendix, 21.)

6. NITROGEN

N.—13.93

Preparation.—The air is mainly a mixture of nitrogen **308** and oxygen, and the removal of the latter gives the most available method of preparing nitrogen.

On a crucible lid, resting on a flat cork, and floating on the water in the tank, place a small piece of phosphorus.

Bringing the cork over the bridge of the tank, ignite the phosphorus and invert a beaker over the latter, letting the beaker rest upon the bridge. The phosphorus burns with a white smoke, which is the pentoxide of phosphorus (P_2O_5), and this is slowly absorbed by the water. The water rises in the beaker, taking the place of the oxygen thus removed, and the gas left is nitrogen. This may be poured upward under water into another beaker or collecting bottle, and the operation repeated until sufficient gas is obtained.

309   **Properties.**—Describe the gas, testing in the usual way as to solubility in water, as to action on red and on blue **310** litmus paper, and as to combustion with the taper.

310/1   NOTE.—Phosphorus must be handled with the greatest care, as it ignites very easily, and burns made by it are very painful and difficult to heal. It should never be cut except while it is under water; the piece to be ignited should be gently touched with filter paper to take up the adhering water. After the generation of nitrogen, any phosphorus left adhering to the lid should be carefully scraped off with the spatula and completely burned, so that there shall be *positively no phosphorus left unconsumed.*

6a. *Nitrogen Monoxide or Nitrous Oxide, N_2O*

312   **Preparation.**—Use the flask fitted with a stopper, and with a rubber and glass delivery tube. Place in this a charge of solid ammonium nitrate, NH_4NO_3, considerably more than enough to cover the bottom of the flask. Support the latter on the asbestos board and iron stand. It is well to pass the neck of the flask through the small ring to prevent its falling over. Apply heat, slowly at first, until a layer of melted salt covers the bottom of the flask. As the heating continues the salt apparently boils; this is really decomposition, and, when it is well started, the flame should be removed lest the action become too violent. Collect the gas over water. Remove the delivery tube from the water before the current of gas ceases. The gas is **313** nitrogen monoxide. Describe it, testing in the usual man-

ner as to solubility, action on litmus paper, and relation to **314**
combustion.

EXPLANATORY NOTE.—Ammonium nitrate is decomposed by heat
into nitrogen monoxide and water, and the reaction liberates heat.
Write the equation.

6b. *Nitrogen Dioxide or Nitric Oxide, NO*

Preparation.—As in Exp. 47/b.   **317**

Examine **as to solubility.**   After shaking in a test-tube **318**
with water, slip a crystal of ferrous sulphate into the test-
tube, opening it under water, and shake again.

As to action on litmus.—This can be observed only by **318/1**
slipping the litmus paper under water into the tube or
bottle containing a sample of the gas, since contact with
air would entirely change its character.

As to combustion.—The usual test with the taper can **318/2**
only be applied in opening the bottle to the air, hence the
observed property really belongs to nitrogen tetroxide or
to a mixture of the two oxides.

Make the combustion test likewise with a piece of
ignited magnesium ribbon.

Save a portion of this gas for the next experiment.

6c. *Nitrogen Trioxide or Nitrous Anhydride, N_2O_3*

No experiments.   **319** to
                                                                   321

6d. *Nitrogen Tetroxide or Peroxide, N_2O_4 or NO_2*

Compare Experiments 47/₁ and 47/₂.

Pass some air into the bottle containing a sample of
nitric oxide.   Note the color, solubility, and action on blue **322** to
litmus paper of the tetroxide thus produced.   **324**

6e. *Nitrogen Pentoxide or Nitric Anhydride, N_2O_5*

No experiments.   **325**

6f. *Nitric Acid, HNO_3*

329   **Preparation.**—It is made by the combination of nitrogen pentoxide and water which takes place on contact; also by adding sulphuric acid to a nitrate—for example, potassium nitrate—and distilling the nitric acid thus liberated from the salt. (See Appendix, 18 B.) What is the other product in this reaction?

331   **Properties.**—Recall the reactions between nitric acid and ferrous sulphate (Exp. 317), and zinc (Exp. 41½) and tin (Exp. 144).

Neutralize about one half test-tubeful of nitric acid from the side table (this is really a solution of nitric acid in water, about 63 per cent) with ammonium hydroxide, concentrate, and crystallize the salt.

331/1   Take a few of these crystals, or, without waiting for these, take some of the substance from the side table, and, heating on the spatula blade, touch a glowing coal to the melted salt.

In similar manner use a few crystals of sodium or potassium nitrate.

331/2   **Nitrohydrochloric acid.**—Cut off a small piece of your platinum wire. Boil this in a test-tube with a few drops of concentrated hydrochloric acid. Does it dissolve? Pour off the acid and try if the platinum dissolves in concentrated nitric acid. Then add to the latter a few drops of hydrochloric acid, and again boil. What evidence of reaction do you see? Does the platinum dissolve?

331/3   Explanatory Note.—In this reaction the hydrogen of the hydrochloric acid is oxidized to water by the nitric acid, chlorine is liberated, and the lower oxide of nitrogen produced. The reaction takes place only when the acids are concentrated, and the solvent action is due to the nascent chlorine. The mixture of the two acids is called nitrohydrochloric acid, or " aqua regia," as it was named in the early days of chemistry because of its powerful solvent action on gold and other metals.

6h. *Ammonia*, NH_3

Preparation.—Heat in a test-tube a piece of flannel or **334** other woolen stuff. Note the odor of the gas and its action on litmus.

EXPLANATORY NOTE.—Wool, hair, and similar organic substances contain nitrogen, as does coal also; these, by dry distillation, yield ammonia or ammonialike substances. Ammonia, therefore, is a product in making illuminating gas by the distillation of coal.

Rub together in the mortar, or even in the palm of the **334/1** hand, some sodium carbonate or some lime and an ammonium salt. What gas is liberated? Write the equation for the reaction.

In a flask fitted with stopper and delivery tube, heat some **334/2** ammonium hydroxide solution. Collect the gas in a dry bottle; it is lighter than air. Is it soluble in water? What **335** is its action on litmus? Does the taper or match burn in the gas? Does the gas itself burn? Test this by holding the tube which delivers the ammonia close to the flame, or by passing the gas into the openings at the base of the chimney. What do you infer are the products when ammonia burns?

7. OXYGEN

O.—15.88

Preparation.—Heat in a test-tube a small quantity of **352** potassium chlorate, $KClO_3$ (about as much as could be heaped on a copper cent). Note the phenomenon, and test the gas at the mouth of the test-tube with a lighted splinter of wood, having care that nothing drops into the test-tube. In a similar manner heat about the same quantity of manganese dioxide. Are you able to get evidence of oxygen at the mouth of the tube? Now mix a little of the chlorate and dioxide, and heat as before and test the gas. Is the gas obtained more readily with or without the dioxide?

To obtain the gas in larger quantity for examination (if the reservoir supply is not at hand), prepare it as in Exp. 71 A, and collect in the smaller bottles.   Recall the results of Exps. 71 A and 71/2.

353 to   Examine as to solubility, action on litmus, and relation
357   to combustion, using a candle or splinter of wood ; and if further illustration is desired, use a bit of sulphur ignited in the metal spoon.

NOTE.—After oxygen is evolved from the chlorate, $KClO_3$, potassium chloride is left. If the temperature is high enough, oxygen is obtained from the manganese dioxide alone, as expressed in the equation

$$3MnO_2 = Mn_3O_4 + 2O.$$

8. FLUORINE

F.—18.91

402   The preparation of this element is difficult, and it is practically impossible as a laboratory experiment.

Its compound with calcium, CaF_2, is a common mineral,
405 known as *calcium fluoride* or *fluor spar*. This is a salt of hydrofluoric acid, HF. By acting upon it with strong sulphuric acid, the former acid is liberated as a gas.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
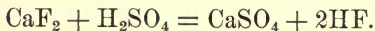
406   The hydrofluoric acid attacks and dissolves glass, and is used practically for etching.   This may be illustrated as follows : Clean and dry a piece of window glass (use one of your glass covers) ; spread over it a thin film of melted paraffin, using the hot spatula blade to melt the latter. With the point of a pin or penknife expose the glass surface by tracing any chosen design through the paraffin. In a shallow lead dish place some powdered fluor spar, and mix this with sulphuric acid to a thin paste. A splinter of wood may serve as stirrer. Cover the dish with the glass plate, the protected side down, and leave for twenty-four hours.

Clean off the paraffin with hot water, and the design will be found etched into the glass. (Scrape the content of the lead dish into the waste jar.)

9. SODIUM

Na.—22.88

The element is supplied already prepared. Describe its **410** appearance. It decomposes water at ordinary temperature. To show this, wet a filter paper, spread it flat on the table, and lay on it a piece of red litmus paper. Place on the filter a piece of sodium, perhaps twice the size of a pin-head. (Have care not to touch sodium with wet fingers.) Describe the phenomenon. If the sodium does not take fire, let a drop of water fall upon it from a glass rod or the end of the finger. Note the action on the litmus. Explain the whole reaction. (Toward the end of the reaction the little globule of melted metal is likely to snap off the paper. Be careful that it is not thrown in the face, or elsewhere, to do harm.)

9c. *Sodium Hydroxide or Caustic Soda*

Recall what is already known of this substance from **420** previous experiments. Describe the solid hydroxide. Make a solution of it, a stick 4 or 5 centimeters long ($1\frac{1}{2}$ or 2 inches), in a beaker one half to three quarters filled with water. Observe what takes place during solution. Neutralize about three quarters of the solution thus obtained with hydrochloric acid, filter, concentrate, and crystallize. What is the appearance of the crystals? What is the substance? Write the equation for the neutralization.

With another portion of the sodium hydroxide solution, **420/1** observe and describe what takes place on adding a few drops of it to dilute solutions of these several salts in different test-tubes: Ammonium nitrate or chloride (heat, and note

odor), iron sulphate, copper sulphate, alum (i. e., aluminium sulphate), sodium nitrate, and perhaps other salts if at hand.

420/2   EXPLANATORY NOTE.—Sodium hydroxide is a base, and it is at least conceivable that, when added to a salt, it might combine with the acid of the latter, forming a new salt and leaving the base of the original salt wholly or partly deprived of its acid—i. e., leaving it in the condition of a hydroxide. Now, if this took place, and if either the new salt or the new hydroxide were insoluble in water, evidence of the change would be seen in precipitation. On the other hand, if the new substances were soluble, no precipitate would appear, and it might be difficult to get evidence as to the change. The fact is that the sodium salts are soluble, but the hydroxides of iron, copper, and aluminium are insoluble, and are the precipitates which are seen in these reactions. Ammonium hydroxide is soluble, hence no precipitate is seen with the ammonium salts; but if the mixture is boiled, ammonia is liberated, showing the presence of the hydroxide in the solution. With sodium nitrate, of course, there is no reaction. The reaction with iron sulphate is expressed in saying sodium hydroxide and iron sulphate become iron hydroxide and sodium sulphate. With this information let the student complete the second, third, and fourth of the following equations, in which the precipitates are underscored:

$$2NaOH + FeSO_4 = \underline{FeO_2H_2} + Na_2SO_4$$
$$NaOH + CuSO_4 = \underline{CuO_2H_2} + Na_2SO_4$$
$$NaOH + Al_2(SO_4)_3 = \underline{Al_2O_6H_6} + 3 Na_2SO_4$$
$$NaOH + NH_4NO_3 = \underline{NH_4OH} + Na NO_3$$
$$NaOH + NaNO_3 = \text{no reaction.}$$
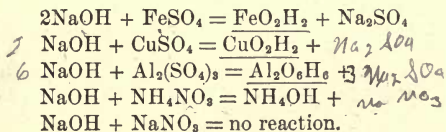
10. MAGNESIUM

Mg.—24.10

445   The element itself is supplied. Describe its appearance and recall whatever has been learned of it in previous experiments. By observation answer the following questions: Does magnesium melt? Does it burn? What is **446** the appearance of the product of combustion, MgO? Does the oxide dissolve in water ? In hydrochloric acid ?

Using strips of the ribbon, one or two centimeters long (one half to three quarters of an inch), ascertain if magnesium decomposes cold water or boiling water. (Have a

piece of red litmus paper in the water.)   Does the hydroxide act as base or acid?   Does the metal dissolve in very dilute hydrochloric acid?   In very dilute nitric acid?   In very dilute sulphuric acid?

Make a dilute solution of magnesium sulphate ($MgSO_4$), **446/1** by dissolving the dry salt (from the side table), a lump about the size of a pea, in a test-tube nearly filled with water.   Add to a small portion of this solution a few drops of sodium hydroxide solution.   What is the precipitate? (See No. 420/2.)   In a similar manner add to different portions of the magnesium sulphate solution a few drops of solutions of these several substances : ammonium hydroxide, ammonium chloride, ammonium carbonate, sodium carbonate, sodium phosphate.   Magnesium hydroxide, carbonate, and phosphate are insoluble.   With this information complete the following equations :

$$Mg + O = \underline{MgO}$$
$$Mg + 2H_2O = \underline{MgO_2H_2} + 2H$$
$$Mg + 2HCl = \underline{MgCl_2} + 2H$$
$$Mg + H_2SO_4 = MgSO_4 + 2H$$
$$MgSO_4 + 2NaOH = \underline{Mg(OH)_2} + Na_2SO_4$$
$$MgSO_4 + Na_2CO_3 = \underline{MgCO_3} + Na_2SO_4$$
$$MgSO_4 + Na_2HPO_4 = \underline{MgHPO_4} + Na_2SO_4$$
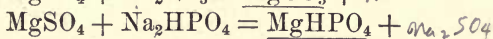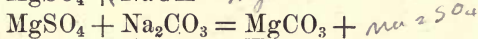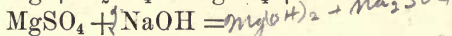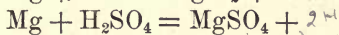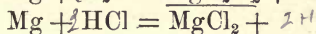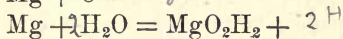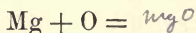
What is the valence of magnesium ?

11. ALUMINIUM

Al.—26.9

The element itself is supplied.   Describe its appearance. **451 to** By trial learn if it melts, and if it burns.   Does it decom- **454** pose water, cold or boiling ?   Does it dissolve in dilute hydrochloric acid?   In dilute nitric ?   In dilute sulphuric ? In dilute solution of sodium hydroxide (boil) ?   What is the behavior of aluminium sulphate (alum) in dilute solution toward these several substances also in dilute solution :

sodium hydroxide (first in small proportion then in excess), ammonium hydroxide, ammonium chloride, sodium carbonate, sodium phosphate? Aluminium hydroxide and phosphate are insoluble in water; the chloride is soluble. The hydroxide dissolves in excess of sodium hydroxide, forming a soluble compound in which the former acts as acid, and the latter as base.

12. SILICON

Si.—28.2

473   EXPLANATORY NOTE.—It is not practicable to supply the element—not, indeed, even to show it. The dioxide, SiO_2, is, however, abundant as common sand. This oxide acts as an acid-former, and when brought in contact with fused sodium carbonate it liberates carbon dioxide and combines with the base, forming a silicate, the composition of which may be sufficiently indicated by the formula Na_2OSiO_2 or Na_2SiO_3. This is soluble in water, and when hydrochloric acid is added to the solution the silicic acid, H_2OSiO_2, in turn is liberated and, being insoluble in water, is precipitated. The precipitate is, however, soluble in the hydrochloric acid, probably without chemical change, and may be reprecipitated by neutralizing the acid, HCl, with ammonium hydroxide.

474   Place a few grains of sand (powdered glass may be used in the same way) in a shallow hole of a piece of charcoal, cover the sand with five or six times its bulk of sodium carbonate, fuse thoroughly, using the blowpipe. Note the minute bubbles. What causes them? After sufficient fusion, remove the mixture from the charcoal, treat with hot water, filter, acidulate with hydrochloric acid, using litmus paper, and boil. If the precipitate does not appear, add ammonium hydroxide to slight alkalinity, and boil again. Describe the appearance of the precipitated silicic acid, H_2SiO_3. Filter the precipitate and dry it.

Complete the equations:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 +$$
$$Na_2SiO_3 + HCl = H_2SiO_3 +$$
$$H_2SiO_3 (heated) = SiO_2 +$$
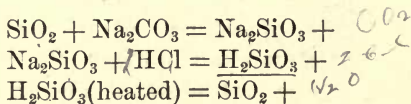
13. PHOSPHORUS

P.—30.8

Recall the use already made of phosphorus. It must be handled with the utmost caution, because of the danger of ignition. Burns produced by it are painful and difficult to heal.

Describe the appearance of yellow phosphorus.   **486**

Place the porcelain lid and cork on a dry glass plate. **487** On the lid place a small fragment of phosphorus. Ignite the latter and cover it with a dry beaker. The oxide formed is mainly P_2O_5. Describe the burning and the product. Let the white oxide settle upon the glass plate. Observe the marked deliquescence. Touch blue litmus paper to the oxide. Is it an acid- or a base-forming oxide?

Phosphorus a reducing agent.—Into a test-tube about one **487/1** third filled with a dilute solution of silver nitrate, $AgNO_3$, drop a small piece of yellow phosphorus, about twice the size of a pinhead. Let stand for twenty-four hours. Minute crystals of metallic silver will be seen at the bottom of the test-tube. The liquid may be drained off and the crystals fused on the charcoal or asbestos to a small globule of silver.

Describe the appearance of the red phosphorus, and **490** compare it with the yellow as to inflammability.

EXPLANATORY NOTE.—Phosphorus pentoxide combines with water **494** to in three different ratios, forming three phosphoric acids, thus: **496**

$$P_2O_5 + 3H_2O = 2H_3PO_4 = \text{orthophosphoric acid.}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 = \text{pyrophosphoric acid.}$$
$$P_2O_5 + H_2O = 2HPO_3 = \text{metaphosphoric acid.}$$
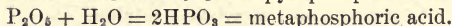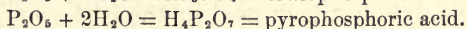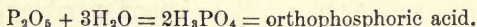
When sodium orthophosphate, Na_2HPO_4, is sufficiently heated, it becomes the pyrophosphate, $Na_4P_2O_7$. Both are soluble in water, but the latter does not immediately pass back to the orthophosphate when in contact with water.

Taking a fragment of crystallized sodium orthophosphate, Na_2HPO_4, fuse it on charcoal, keeping it fused for some minutes. Remove the salt when cool, dissolve in a

little hot water, filter, and to the solution add a few drops of silver nitrate solution. Describe the precipitate, $Ag_4P_2O_7$. Dissolve a small piece of the sodium orthophosphate in water, and add to this a few drops of silver nitrate. Describe this precipitate, Ag_3PO_4. How has the fusion changed the orthophosphate? Write the equation for the reaction of fusion, also for the precipitations.

14. SULPHUR

S.—31.83

509   **Sulphur** was studied in considerable detail at the very first of the course, and it would seem unnecessary to repeat the experiments here. They should at least be recalled, and it may be well to write out a description from the earlier observations. These items may serve as outline : specific gravity, as to solubility in water, color, hardness, crystalline form from fusion, from solution in carbon disulphide, plastic allotropic form, fusion, combustion, behavior with iron, with zinc, and with lime.

510   **Hydrogen sulphide,** H_2S, also was studied somewhat, and these items
and   should be recalled : formation by the action of hydrochloric acid on
511   metallic sulphides, odor of gas, action on paper wet with lead acetate, behavior with strong nitric acid.

512   **The sulphides.**—Hydrogen sulphide is an acid, and in combining with ammonium hydroxide it forms the acid sulphide, NH_4HS, or the normal $(NH_4)_2S$. Persulphides also are formed, such as $(NH_4)_2S_2$ and $(NH_4)_2S_3$, the coefficient of S being 2 or more. The common reagent, yellow ammonium sulphide, much used in the laboratory, is made by saturating ammonium hydroxide with the gas, H_2S. It therefore contains more or less persulphide. With this solution of ammonium sulphide make the following experiments and describe the results : Add a small portion to these several solutions : hydrochloric acid, sodium nitrate, magnesium sulphate, alum, iron sulphate, copper sulphate, lead acetate, and, if at hand, to solutions containing arsenic, antimony, and cadmium.

Complete the following equations:

$(NH_4)_2S + 2HCl =$ *2 NH₄Cl + H₂S* [handwritten]

$(NH_4)_2S_2 + 2HCl =$ *2S + (NH₄)... 2 NH₄Cl + H₂S* [handwritten]

$(NH_4)_2S + 2NaNO_3 =$ *2 NaNH₃ + NaₐS O* [handwritten]

$(NH_4)_2S + MgSO_4 =$ *0* [handwritten]

$(NH_4)_2S + Al_2(SO_4)_3 = Al_2O_6H_6 +$ *H₂O* [handwritten]

$(NH_4)_2S + FeSO_4 = \underline{FeS} +$ *(NH₄)₂SO₃* [handwritten]

$(NH_4)_2S + CuSO_4 = \underline{CuS} +$
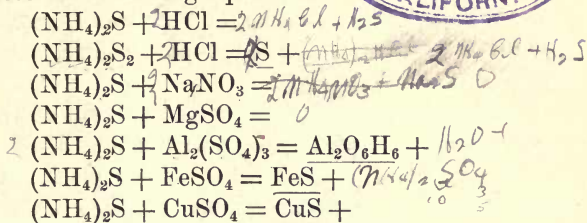
What is the valence of sulphur in hydrogen sulphide?

Sulphur dioxide.—This substance is formed by burning **515**
sulphur, but more conveniently by the action of hydro-
chloric acid on sodium sulphite, Na_2SO_3. Place some of
the latter in the generator, add the acid gradually, and
collect the gas by dry displacement, since it is soluble in
water and heavier than air. Test the gas for odor (it is **516**
very irritating), solubility, action on the burning candle or
match, weight as compared with air (as in the experiment
with carbon dioxide No. 263), and action on litmus paper,
both brief and somewhat prolonged.

To a portion of sodium sulphite solution add a few **517**
drops of potassium permanganate, $KMnO_4$, and to another
portion add a crystal of iodine. Describe what takes place.

Sulphur dioxide, sulphurous acid, H_2SO_3, and the sulphites, all tend
more or less readily to take up oxygen and become the trioxide, sul-
phuric acid, H_2SO_4, and the sulphates respectively; the former there-
fore act as reducing agents.

Complete these equations: **517/1**

$S + O =$ *SO₂* [handwritten]

$SO_2 + H_2O =$ *H₂SO₃O* [handwritten]

$H_2SO_3 + 2NaOH = Na_2SO_3 +$ *2 H₂O* [handwritten]

$Na_2SO_3 + 2HCl =$ *SO₂ + H₂O + 2 Na Cl* [handwritten]

$SO_2 + O =$ *SO₃* [handwritten]

$H_2SO_3 + O =$ *H₂SO₄* [handwritten]

$Na_2SO_3 + O =$ *Na₂SO₄* [handwritten]

$Na_2SO_3 + H_2O + 2I = 2HI +$ *Na₂SO₄* [handwritten]

$Na_2SO_3 + K_2O.Mn_2O_7 + H_2O = 2KOH + 2MnO +$ *Na₂SO₄* [handwritten]

23
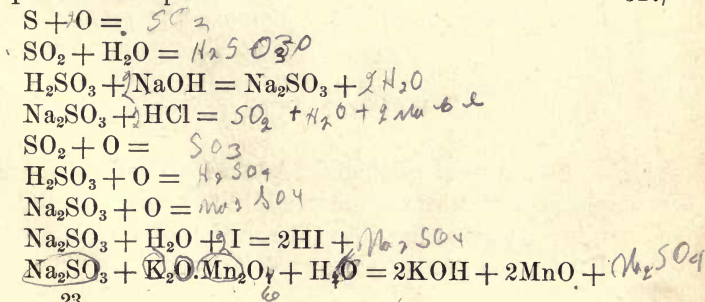
519   **Sulphuric acid.**—With sulphur trioxide it is not practicable to work, but its compound with water, *sulphuric acid*, $H_2O.SO_3$, or H_2SO_4, is a common reagent. Describe its appearance.

Taking about one half of a test-tubeful of the concentrated sulphuric acid, dilute it with about three times its volume of water. Note what takes place. CAUTION : *Make it a rule in diluting strong sulphuric acid always to add the acid to the water slowly and with constant stirring, and never the water to the acid.* Why?

521   Taking three equal portions of the dilute acid, neutralize one portion with a solution of sodium hydroxide, filter, concentrate, and crystallize. Neutralize the second portion in the same way, and to it add the third portion; filter, concentrate, and crystallize. Compare the crystallizations; dry a sample of each product on filter paper, and test it with litmus paper, red and blue. Let a sample of each lie exposed to the air for twenty-four hours.

519/1   To show the tendency of strong sulphuric acid to remove the constituents of water : having a small quantity of the acid in a test-tube, drop into it a splinter of pine wood, or a piece of filter paper. What takes place after some minutes?

521/1   Sulphate changed to sulphide : taking a crystal of sodium sulphate from the side table or from the product of the preceding experiment, No. 521, fuse it on the charcoal, first adding some sodium carbonate (use the reducing flame of the blowpipe). Remove the product from the charcoal, lay it upon a piece of filter paper wet with lead acetate, and let a drop of water fall upon it. What does the black stain indicate? A silver coin may be substituted for the lead paper.

521/2   **Solubility of sulphates.**—Add a few drops of sodium sulphate or of dilute sulphuric acid to a solution of lead acetate; also, if at hand, to the solution of a barium salt (e. g., $BaCl_2$), and of a strontium salt (e. g., $SrCl_2$).

Complete these equations:

$$SO_3 + H_2O =$$
$$H_2SO_4 + NaOH = Na_2SO_4 +$$
$$H_2SO_4 + NaOH = NaHSO_4 +$$
$$Na_2SO_4 + C = Na_2S + CO_2$$
$$H_2SO_4 + BaCl_2 = \underline{BaSO_4} +$$
$$Na_2SO_4 + SrCl_2 = \underline{SrSO_4} +$$
$$Na_2SO_4 + Pb(A)_2 = \underline{PbSO_4} +$$
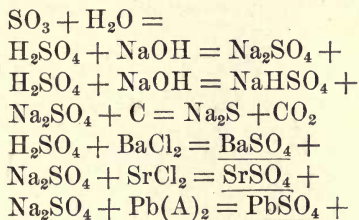
15. CHLORINE

Cl.—35.18

This element is extremely disagreeable to deal with in large quantity. It is best that the illustrative experiments in the laboratory be only on the test-tube scale.

Preparation.—Hydrochloric acid is commonly the source **529** of chlorine. From this it is obtained by oxidizing the hydrogen to water, and thus liberating the chlorine. The methods differ only in the means used to oxidize.

(*a*) Place in a test-tube a small quantity of manganese **529/2** dioxide, MnO_2, about as much as could be heaped on a copper cent. Add to this about one quarter of a test-tubeful of concentrated hydrochloric acid and warm gently. Observe cautiously the odor, also the effect on wet litmus **530** paper of brief and then of somewhat prolonged exposure to the gas. Enough of the gas may be generated in the test-tube to show its color, and some of it may be poured into a second dry tube (it is heavier than air) in order to test as to its solubility in water.

Complete this equation by inserting the necessary coefficients:

$$MnO_2 + \quad HCl = MnCl_2 \text{ (sol. salt)} + \quad H_2O + \quad Cl.$$
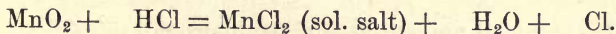
(*b*) Place in a test-tube some potassium chlorate, $KClO_3$, **529/1** about the size of a pinhead, and add concentrated hydrochloric acid, a few drops. Note the evolution of gas, the

odor, color, etc. Dilute with water. Does the reaction continue? Complete the equation:

$$KClO_3 +   HCl = KCl \text{ (sol. salt)} +   H_2O +   Cl.$$
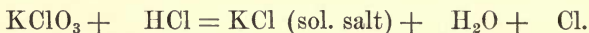
Hydrochloric Acid, HCl

534   **Preparation.**—Place some sodium chloride, NaCl, in a test-tube; a lump about the size of a pea will serve. Add to this a few drops of concentrated sulphuric acid, H_2SO_4, and warm. Note the odor of the gas, and its action on blue litmus paper. Hold at the mouth of the test-tube a glass rod wet with ammonium hydroxide. What causes the white fumes?

The properties of hydrochloric acid have been illustrated in its repeated use.

534/1   **Solubility of chlorides.**—Mix a few drops of hydrochloric acid, or of sodium chloride solution, with these several salts in dilute solution: lead acetate, $Pb(C_2H_3O_2)_2$; silver nitrate, $AgNO_3$; mercurous nitrate (if at hand), $HgNO_3$; magnesium sulphate, $MgSO_4$; iron sulphate, $FeSO_4$, etc. The first three of these bases form insoluble chlorides. The other chlorides are as a rule soluble.

Complete these equations:

$$NaCl + H_2SO_4 =$$
$$HCl + Pb(C_2H_3O_2)_2 =$$
$$HCl + AgNO_3 =$$
$$HCl + HgNO_3 =$$
$$HCl + MgSO_4 =$$
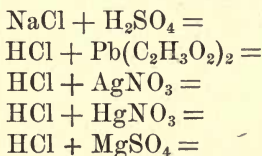
16. POTASSIUM

K.—38.82

552 and 553   If the metal potassium and its hydroxide, KOH, are at hand, experiments with them may be made exactly as with sodium and sodium hydroxide. But the results are so entirely similar that the observations may be omitted.

17. CALCIUM

Ca.—39.7

The element is not available for these experiments, **581** being difficult to obtain, but the oxide, lime, CaO, is readily procured.   If quicklime is at hand, use it to observe the effect of contact with water.   If only slaked lime, $Ca(OH)_2$, is provided, it will serve, except for this single observation.   Learn by experiment if calcium hydroxide dissolves **582** in water.   Does it act as base or as acid ?   What reaction takes place with carbon dioxide ?   Prepare a solution of calcium chloride, $CaCl_2$, by neutralizing with lime about one third of a test-tubeful of the acid, and filtering.   With **584** this solution, observe the reactions with dilute solutions of these several substances : ammonium hydroxide, chloride, carbonate, and oxalate $(NH_4)_2C_2O_4$; sodium phosphate, and sodium or potassium sulphate or dilute sulphuric acid. Complete the following equations :

$$CaO + H_2O = \quad \text{[handwritten: } CaO_2 + 2H]$$
$$Ca(OH)_2 + CO_2 = \quad \text{[handwritten: } CaCO_3 + H_2O]$$
$$Ca(OH)_2 + HCl = \quad \text{[handwritten: } Ca\,Cl +]$$
$$CaCl_2 + (NH_4)_2CO_3 = \quad \text{[handwritten: } CaCO_3 + (NH_4)_2Cl \quad 2\,NH_4Cl]$$
$$CaCl_2 + (NH_4)_2C_2O_4 =$$
$$CaCl_2 + Na_2HPO_4 =$$
$$CaCl_2 + Na_2SO_4 =$$
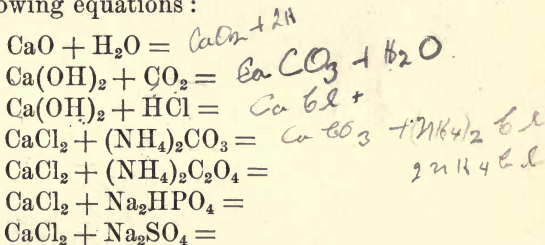
23. IRON

Fe.—55.6

Several experiments with iron and its salts have already **596** been performed, and should be recalled here.   With a sample of iron, learn by trial if it melts or burns in the flame of the Bunsen burner or in that of the blowpipe.   Does it decompose water, cold or boiling ?   Does it dissolve in **598** dilute hydrochloric acid (recall other experiments) ?   In dilute nitric acid ?   In dilute sulphuric acid ?

Take about a test-tubeful of hydrochloric acid, dissolve in this as much iron as it will take up, keeping some excess of iron present (a nail serves well). Filter, concen-

600 trate, and crystallize the ferrous chloride.

As alternative with the preceding, dilute sulphuric acid may be used and the ferrous sulphate may be crystallized.

To a dilute solution of ferrous salt freshly made, add ammonium hydroxide solution. What is the precipitate?

600/1 To a dilute solution of ferrous salt add a few drops of concentrated nitric acid, boil a few seconds, then add ammonium hydroxide to alkaline reaction. What is the pre-

601 cipitate? [Ferric hydroxide, $Fe_2(OH)_6$ or $Fe(OH)_3$, similar to iron rust.] What takes place when solution of ammonium sulphide is added to a ferrous solution? Recall the experiment made previously in studying the sulphides.

EXPLANATORY NOTE.—The ferrous salts when in solution oxidize readily to ferric salts even by the action of the air, more quickly by the action of nitric acid. The color changes in consequence, and the precipitates with ammonium hydroxide and other reagents are different.

Complete the following equations :

$$Fe + HCl = FeCl_2 +$$
$$Fe + H_2SO_4 = FeSO_4 +$$
$$FeSO_4 + HNO_3 = Fe_2(SO_4)_3 + NO +$$
$$FeCl_2 + NH_4OH = Fe(OH)_2 +$$
$$FeCl_2 + NH_4HS = FeS +$$
$$FeCl_3 + NH_4HS = FeS +$$
$$FeCl_3 + NH_4OH = Fe(OH)_3 +$$
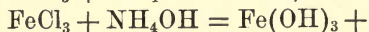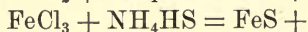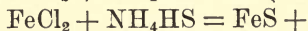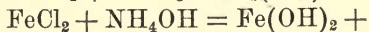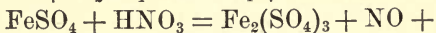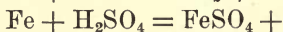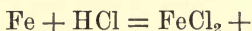
APPENDIX

Weighing.—Substances which corrode metal should be [1] weighed on glass, and general care should be taken to protect the metallic parts of the balance from injury. Things when weighed should not be hot, but should be at the temperature of the room. During the more exact weighing, care should be taken that currents of air do not interfere with the swinging of the beam. The equilibrium should be tested while the beam is in motion by the equality of swing to either side of the zero point, *S*, on the scale. Generally the equilibrium should be tried with nothing in the pans before the actual weighing. In using balances of the type A or B (Fig. 5 or Fig. 6), it is best to put the object to be weighed on the left-hand pan, and the weights, or counterpoise, on the right. The weights should be placed in the pan for trial in regular succession, until one is found which is too heavy and one which is too light, and finally the exact counterpoise is found. It is well to read the weights first from the vacant places in the box, record the total, then read from the weights themselves as they are taken from the pan, the largest first. Care must be taken to return each weight to its proper place, to guard against the loss of any, and to leave the balance clean and in proper condition for the next weighing.

The balance of the type A is for the heavier weighings, and will hardly respond to less than 0.2 or 0.3 of a gram. The balance B should indicate 0.01 of a gram. The equilibrium is tested by pressing down the lever, *L*, which raises
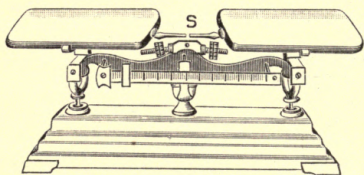
Fig. 5.—Balance A.
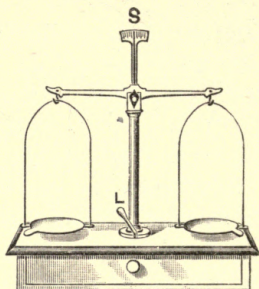
Fig. 6.—Balance B.
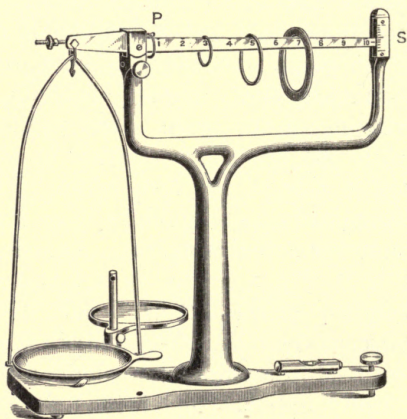
Fig. 7.—Balance C.

Weights.
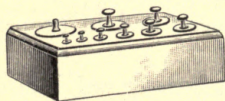
Fig. 8.
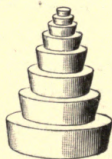
Fig. 9.
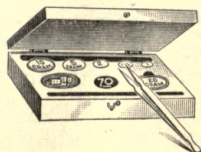
Fig. 10.

the beam so that it is free to swing. The balance C has but one pan, and the weights are in the form of rings which slide along the beam without removal therefrom, but when not in use hang upon the peg, *P*. The largest ring gives grams in tens, the next smaller in units, the third in tenths, and the fourth in hundredths. So the total reading shown in the figure is 75.30 grams.

Heating a test-tube, Fig. 11.—A strip of paper is folded 2 two or three times upon itself and wrapped around the test-tube to serve as holder, or, better, a strip of asbestos is thus used.
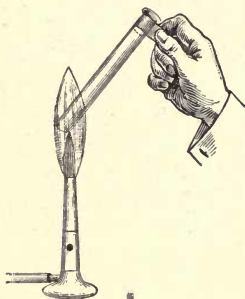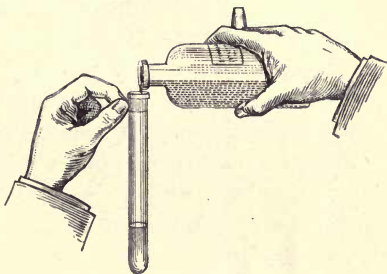
FIG. 11.   FIG. 12.

Pouring from a reagent bottle, Fig. 12.—The stopper is 3 taken between the fingers of the right or left hand as preferred, and withdrawn from the bottle. This is to avoid laying the stopper on the table.

Inverting and shaking a test-tube, Fig. 13.   4

The mortar and pestle, Fig. 14.   5
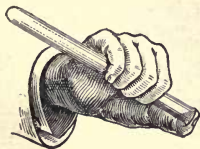
FIG. 13.   FIG. 14.

6   *The gas generator*, Fig. 15.—*T*, Thistle-tube; *D*, delivery tube. It is well to wet glass tubing when putting it through stoppers or connecting it with rubber hose.

7   *To cut glass tubing.*—Make a scratch with a three-edged file where it is desired the tube shall break. Hold the tube in both hands, the thumbs brought together on the opposite side from the scratch. Pull the hands apart in the direction of the tube's axis, with only a *very slight* bending motion. If the tube is short or the glass thin, it is well to hold it in one or two folds of the towel. Fig. 16.

8   *To smooth the sharp edge* of a cut tube, hold the end in the gas flame until the glass softens. Fig. 17.

9   *To bend* glass tubing, hold it in the flame, preferably a wide one, twirling it between the thumb and fingers until the glass is thoroughly softened, then slowly bend to the desired angle. The bend should be smoothly curved, as seen in the figure. If the heating is insufficient, or the bending too hasty, the glass wrinkles, and the tube is likely to break. It is well to pass the tube through the flame once or twice after it is bent, so that the cooling may be slow. Fig. 18.

10   *To draw out and close* glass tubing, hold it in the flame until the glass is well softened, then draw apart slowly and to the desired extent, and finally heat it still more at the separating point and draw again. Fig. 19.

11   *Heating a crucible*, Fig. 20.—The crucible, *C*, rests on the pipestem triangle, *T*, and this in turn on the iron ring of the stand, *S*. The tongs, *X*, are used to handle the crucible or its lid while hot.

12   *Evaporation to dryness in the porcelain dish*, *D*, Fig. 21.—When there is danger of spattering, it is well to hold the burner in the hand, and to touch the tip of the small flame for a moment to the bottom of the dish. The purpose is to heat, but not enough to cause the formation of bubbles of vapor. Constant stirring with the rod, *R*, is important.
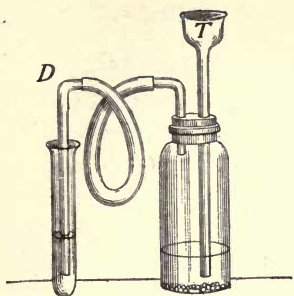
FIG. 15.
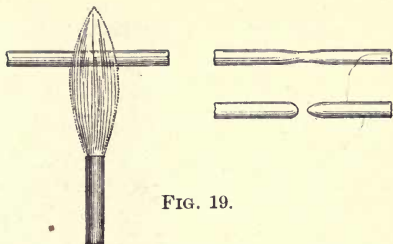
FIG. 19.

FIG. 16.

FIG. 17.

FIG. 20.

Good.   Bad.
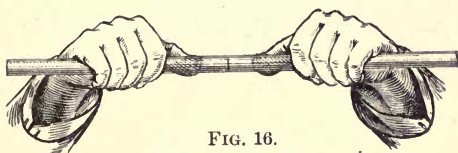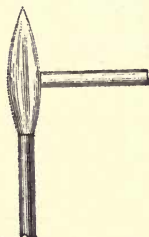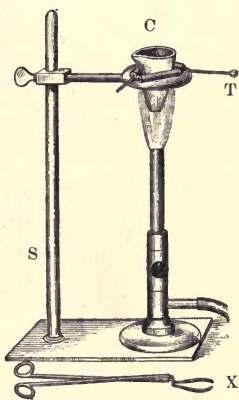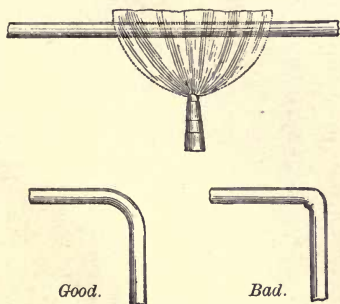
FIG. 18.
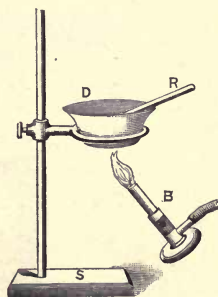
FIG. 21.

13   *Filtration.*—Prepare the filter paper by folding it across two diameters at right angles to each other, then separating the quadrants so as to form a cone, *d.* The cone should be fitted into the funnel and then wet, so that the paper adheres to the glass.   Fig. 22.

Fig. 23.—Filtering, pouring the liquid from the beaker, *B*, using the rod, *R*, upon the funnel, *F*; showing the stem of the funnel lying against the wall of the beaker, so that the liquid which runs through may not cause spattering by dropping into the middle of the beaker.

14   *The graduated cylinder*, Fig. 24, to use in measuring liquids; content, fifty cubic centimeters (c. c.).
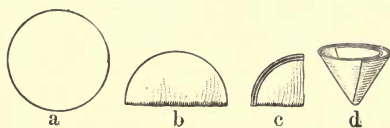
Fig. 22.
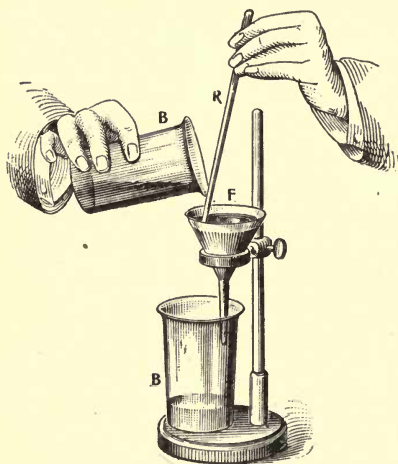
Fig. 23.

Fig. 24.

The thermometer.—The measurement of temperature **15A** is made with the centigrade thermometer. The fixed points of this are the boiling point of water and the melting point of ice. The latter is made 0° of the scale, and the former is made 100°, the space between the two points being divided into one hundred equal parts, called degrees. In the Fahrenheit thermometer, which is more commonly used in matters other than scientific, these two points are made 32° and 212° respectively. The relation between the two scales is made clear in the diagram. Fig. 25.

Thermometers are fragile and expensive, and must be used with care.
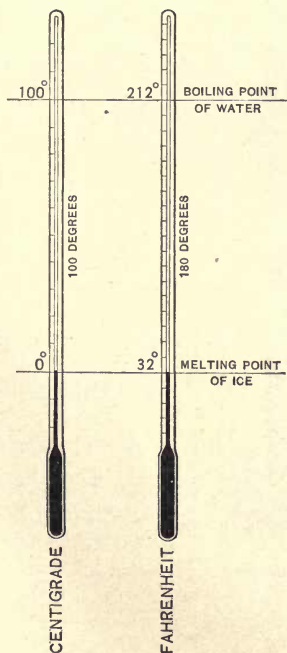
FIG. 25.

15B   *The barometer*, Fig. 26.—The long tube is completely filled with mercury, then inverted in the shallow dish of mercury. The atmospheric pressure on the free surface of the mercury sustains a column of varying length, the normal being 760 millimeters. Fig. 27, the siphon form of barometer.

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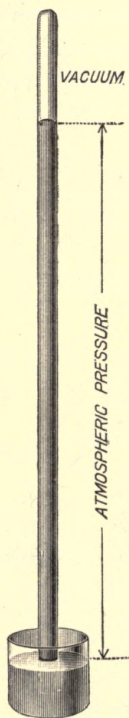
Fig. 26.

Fig. 27.

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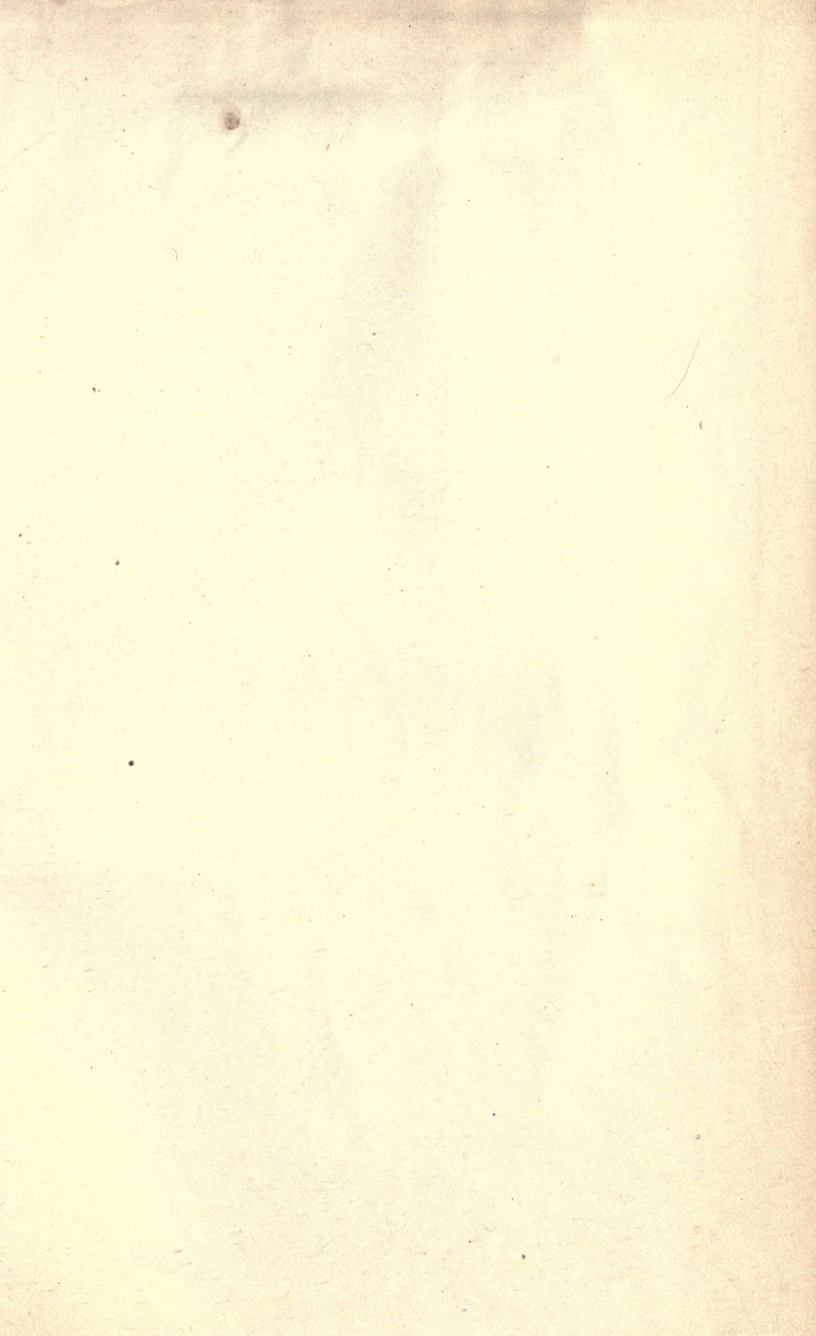
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